

CA1 HW 1179E45

CA1 HW1179 E45

Canada. DNHW. EHD.

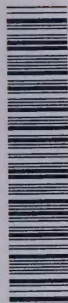
79-EHD-45

THE REMOVAL OF ORGANICS FROM DRINKING WATER BY
OZONATION, BIODEGRADATION AND ACTIVATED CARBON
ADSORPTION. 1979. The Removal of Organics from Drinking
Water by Ozonation, Biodegradation and Activated Carbon
Adsorption.

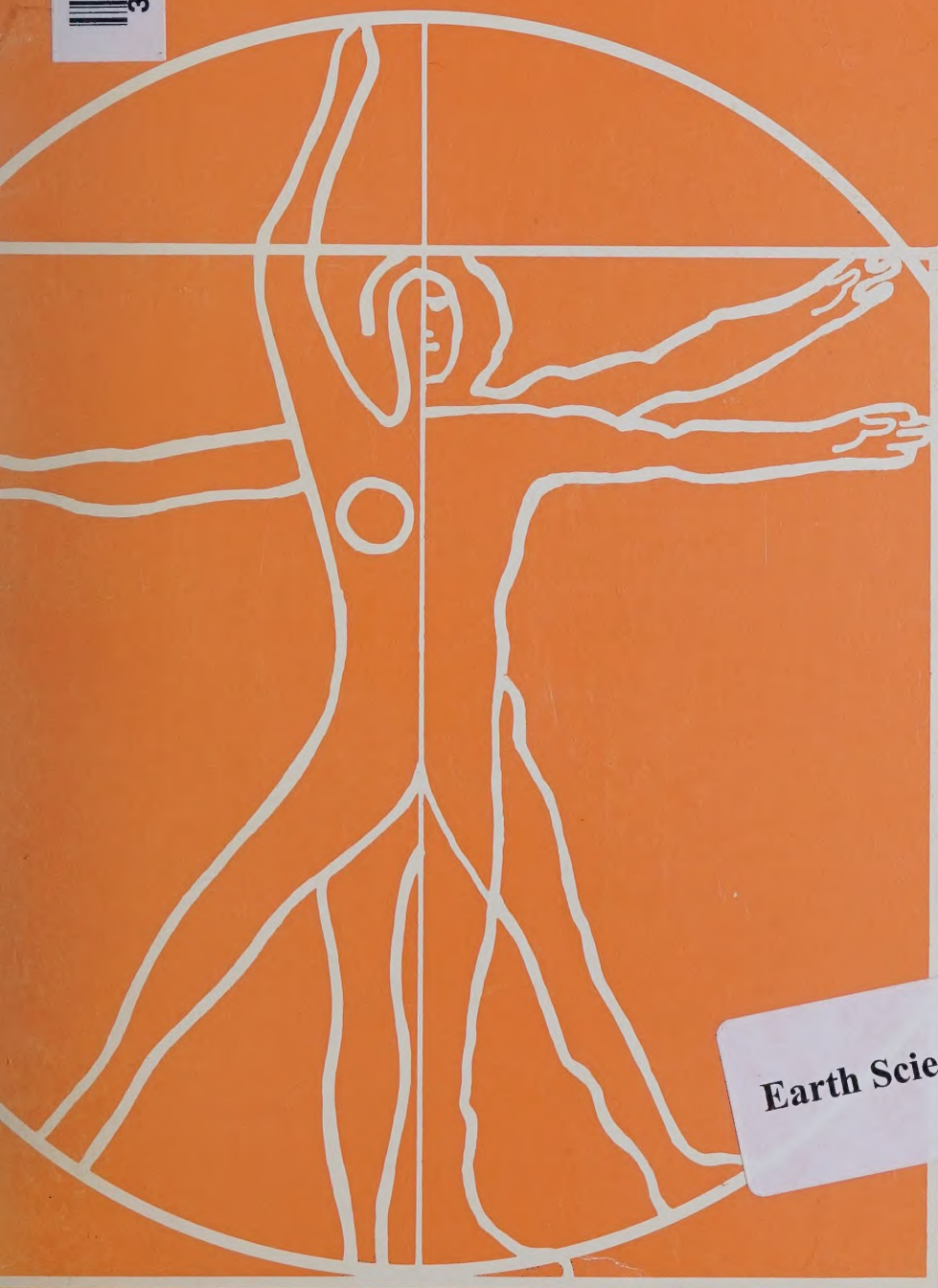
santé et Bien-être social
Canada

CA1 HW1179 E45

Removal of organics from drinking water by ozonation, biodegradation and activated carbon adsorption



3 1761 05688780 5



Earth Sciences Library



Digitized by the Internet Archive
in 2025 with funding from
University of Toronto

<https://archive.org/details/31761056887805>

THE REMOVAL OF ORGANICS FROM DRINKING WATER
BY
OZONATION, BIODEGRADATION AND ACTIVATED CARBON ADSORPTION

ENVIRONMENTAL HEALTH DIRECTORATE
HEALTH PROTECTION BRANCH

PUBLISHED BY AUTHORITY OF THE
MINISTER OF NATIONAL HEALTH
AND WELFARE

COPIES OF THIS REPORT
CAN BE OBTAINED FROM:

INFORMATION DIRECTORATE
DEPARTMENT OF NATIONAL HEALTH
AND WELFARE
BROOKE CLAXTON BUILDING
OTTAWA K1A 0K9

THIS DOCUMENT WAS PREPARED UNDER CONTRACT BY:

FENCO CONSULTANTS LTD.

DR. A. BENEDEK, PRINCIPAL INVESTIGATOR,
MCMASTER UNIVERSITY

MR. E.A. LANCASTER, PRINCIPAL COINVESTIGATOR,
FENCO CONSULTANTS LTD.

MR. J.J. BANCSEI, RESEARCH ENGINEER,
MCMASTER UNIVERSITY

MR. P. STEPHENSON, GRADUATE STUDENT,
MCMASTER UNIVERSITY

NOVEMBER 1979

THIS IS REPRODUCED AS RECEIVED FROM THE CONTRACTOR.
THE CONCLUSIONS AND RECOMMENDATIONS CONTAINED HEREIN
REPRESENT THE OPINION OF THE CONTRACTOR AND DO NOT
NECESSARILY CONSTITUTE ENDORSEMENT BY THE DEPARTMENT
OF NATIONAL HEALTH AND WELFARE.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	i
SUMMARY	ii
RECOMMENDATIONS	v
ACKNOWLEDGEMENTS	vi
1. INTRODUCTION	1
2. EXPERIMENTAL	5
2.1 Water Sampling Programme	5
2.2 Ozonation Apparatus and Procedure	5
2.3 Biodegradation Apparatus and Procedure	9
2.4 Adsorption Isotherm Apparatus and Procedure	12
2.5 Continuous Flow Adsorption Apparatus and Procedure	13
2.6 Outline of Analytical Methods	15
3. RAW WATER AND PRETREATED WATER CHARACTERISTICS	17
3.1 Raw Water Characteristics	17
3.2 Pretreated Water Characteristics and the Effect of Pretreatment	20
4. OZONATION STUDIES	27
4.1 TOC Removal	27
4.2 Selectivity in Organic Removal and Partial Oxidation	30
5. BIODEGRADATION STUDIES	35
5.1 Oxygen Uptake	35
5.2 Organic Removal	37
6. ACTIVATED CARBON ADSORPTION STUDIES	41
6.1 Adsorption Isotherm Studies	41
6.2 Continuous Flow Studies	49
7. OVERALL ORGANIC REMOVALS	60
8. CONCLUSIONS	63

	<u>Page</u>
REFERENCES	65
Appendix A: Detailed Analytical Methods	69
B: Tabulated Data	79
C: Biodegradation Data	89
D: Adsorption Data	99
E: Partial Oxidation of Organics	123

ABSTRACT

The combination ozonation-biodegradation-carbon adsorption has found wide use in the newer drinking water treatment plants of Western Europe. This process combination, added on to the end of the treatment train of a conventional North American water treatment plant would be expected to significantly improve organic removal. This study has been designed to verify the above expectations by batch and bench scale continuous studies of ozonation, biodegradation and activated carbon adsorption. The results indicate that this process combination is indeed capable of removing organic substances, including synthetic organics such as polycyclic aromatic hydrocarbons and halogenated organics to desired levels.

RÉSUMÉ

Les nouvelles usines de purification des eaux de boisson de l'Europe de l'Ouest font largement appel à l'utilisation réunie de l'ozonisation, de la biodégradation et de l'adsorption sur charbon. Cet ensemble de procédés, utilisé à la suite des opérations effectuées dans les usines de traitement des eaux classiques de l'Amérique du Nord, devrait permettre d'améliorer de façon importante l'élimination des matières organiques. La présente étude a été conçue dans le but de vérifier ces attentes par des essais en laboratoire, en discontinu et en continu, portant sur l'ozonisation, la biodégradation et l'adsorption sur charbon activé. Les résultats obtenus montrent que l'utilisation réunie de ces procédés peut vraiment permettre d'éliminer des substances organiques, y compris des matières organiques synthétiques comme des hydrocarbures aromatiques polycycliques et des matières organiques halogénées, de façon à atteindre les teneurs désirées.

SUMMARY

This study was designed to examine the removal of organics found in potable water by ozonation, biodegradation, and carbon adsorption. The study consisted of batch and semi-continuous studies. During the batch studies, samples were brought from the Grand River and pretreated by coagulation, sedimentation and sand filtration. The pretreatment stage is analogous, with the exception of chlorination, to the conventional type of treatment practised in North America. Subsequently, the samples were ozonated at different applied dosages. Each ozonated sample (including a zero ozone dose sample) was then treated by the addition of bacterial seed in a respirometer. Biodegradation was continued in the respirometer until oxygen up-take ceased. Carbon adsorption isotherms were conducted after ozonation as well as after ozonation-biodegradation treatments. Seven water samples, abstracted at different times (ranging from September 1978 to March 1979) were treated in this fashion. During the later part of the study, a set of pilot continuous flow adsorption columns were also run. In these semi-continuous experiments, the continuously run column feed was prepared in batchwise fashion up to the ozonation stage.

The removal of organics was determined in terms of several lumped organic parameters such as Total Organic Carbon (TOC),

Chemical Oxygen Demand (COD), and Absorbance at 254 nm in a 10 cm cell ($A_{254\text{nm}}^{10\text{ cm}}$). Furthermore, special attention was paid to two specific groups of synthetic organics. First, Polycyclic Aromatic Hydrocarbons (PAH) were analyzed individually and then summed for the lumped group parameter, ΣPAH . Second, total non-polar halogenated organics were also determined as TOX.

The results indicate that coagulation, sedimentation and filtration removes a substantial portion of the organics (approximately 35% of the TOC). Subsequently, almost all remaining organics can be removed by the combination of ozonation, biodegradation and activated carbon adsorption. Ozonation is very efficient in removing PAH, even at levels as low as 2 mg/l of ozone, however, it is inefficient for TOC removal. TOC removal is best accomplished by biodegradation plus adsorption. The level of halogenated organics, without chlorination, was generally low in this water supply. As the levels observed were near the detection limit of the TOX method, the results for TOX removal by specific treatment steps are not reliable.

In general, ozonation improved the biodegradation of the organics without significant alteration in their sorption characteristics on carbon. However, little of this improvement

was observed to occur in the continuous adsorption experiments. In these experiments organic removal was believed to occur by adsorption primarily. Thus organic removals were slightly better without preozonation.

It was found that a shock load of orthochlorophenol was completely damped out by the continuous flow adsorption columns, thereby indicating the utility of adsorption beds for the protection of water consumers from accidental high level contamination in the water supply.

RECOMMENDATIONS

The following recommendations can be made on the basis of this study:

- (i) The results of the study should be extended to cover other types of water supply.
- (ii) Pilot plant studies should be carried out at chosen sites to determine scale-up parameters.
- (iii) Engineering cost estimates should be prepared on the basis of the results of parts (i) and (ii) for typical Canadian water supplies.

ACKNOWLEDGEMENTS

Dr. M. Malaiyandi of Health and Welfare Canada has provided consistent technical support throughout the duration of this study.

Acknowledgement is also due to Dr. O. Meresz, Dr. R.D. Smillie and Mr. D.T. Wang of the Trace Organics Laboratory of the Ontario Ministry of the Environment for their help in PAH analysis.

Thanks are also due to Mr. M. Schwartz of FENCO Consultants Ltd. for proposing this study and for his efforts in its initial implementation.

1. INTRODUCTION

The presence of synthetic organics in drinking water has been well documented by the Municipal Research Laboratory of the U.S. Environmental Protection Agency, which had, at last count, identified over 600 organic compounds of industrial origin in U.S. drinking waters, (Shackelford and Keith, 1976). Canadian research by the Bureau of Chemical Hazards, Health and Welfare Canada identified many such compounds in Canadian drinking water, (Benoit et al, 1979).

Most of the organics identified in these drinking waters are believed to be present in the original water source although some of the identified chlorinated organics, particularly the trihalomethanes, have been shown to be accidentally synthesized, during water treatment, when chlorine is used as a disinfectant. Water treatment plants in Canada often produce as much as 200 µg/l of trihalomethanes (Nicholson and Meresz, 1976) and an unknown quantity of higher molecular weight chlorinated organics. The presence of these organics is considered to be potentially harmful to the consumer's health. Furthermore, some of the chlorinated organics produced during water treatment probably accumulate in wildlife while others may be recycled as a potable water contaminant. Accordingly, a need exists

to limit the presence of synthetic organics in drinking water and the production thereof during the water treatment process.

North American water treatment processes are primarily designed to control bacterial contamination within stringent limits and to improve the aesthetic quality of the water for human consumption. Until recently, little if any attention has been paid to the minimization of synthetic organics. In Europe, drinking water is often derived from polluted rivers such as the Rhine and Seine, in which the levels of synthetic organics are relatively high. As a result, modern European plants frequently use the combination of ozonation and activated carbon adsorption to reduce synthetic organics. In such plants the ozone serves two functions. It disinfects the water and also renders some of the synthetic organics more amenable to biodegradation and removal during the subsequent treatment step of activated carbon adsorption. At the same time, more persistent and refractory organics are adsorbed. Thus the combination, pre-ozonation-biodegradation-activated carbon adsorption, is able to provide good disinfection, a significant reduction in organic content and, generally, drinking water which is palatable in terms of odour, taste and appearance. Furthermore, as much of the organic reduction occurs through biological means, the activated

carbon beds are regenerated rather infrequently and, therefore, the process can be and generally is relatively inexpensive.

It is perhaps important to note that Europeans, in many cases, still provide post-chlorination of the ozone disinfected water in order that a residual disinfectant should be present in the tap water. This post-chlorination, however, does not result in the relatively high levels of chlorinated organics often encountered in Canadian drinking water (Schalekamp, 1975). In all probability, this is due to the lower level of potential organics present after biological activated carbon treatment. It may also be due to the fact that Europeans tend to require lower chlorine residual levels in their potable water supplies which could account, in part, for the lower levels of trihalomethanes generally encountered in such waters.

In Canada, the number of treatment plants employing ozone is small but appears to be increasing. In most such cases, the use of ozone is primarily for colour and odour reduction, with side benefits in terms of disinfection also being obtained. In all such cases, however, post-chlorination is employed to ensure both effective and persistent disinfection in the transmission and distribution lines.

As indicated earlier, up to the present time there has not been a systematic attempt to apply some of the more advanced European water treatment processes to Canadian water supplies. The Environmental Health Directorate of Health and Welfare Canada sponsored this project to evaluate the applicability of the biological activated carbon process to the reduction of synthetic organics in one industrially-polluted river water supply.

More specifically, the overall objectives of this study were as follows:

- (i) to determine the organic removal process capabilities and optimum processing conditions of the ozonation-biodegradation-carbon adsorption process combination.
- (ii) to determine the level of key or indicator synthetic organic compounds and to study their removal in the ozonation-biodegradation-carbon adsorption process.

2. EXPERIMENTAL

2.1 Water Sampling Programme

A total of seven samples were abstracted from the Grand River of Southern Ontario (see Figure 2.1-1).

The majority of organics found in this river originate from the bacterial breakdown of vegetative matter that takes place in the upper reaches of the river. By the time the river reaches the sampling point for this study, the river also receives a substantial input of domestic and industrial wastewaters from the Kitchener-Waterloo area and the organic residues from these wastewaters are expected to contribute to the level of organics in the river.

Samples were taken by pumping river water directly into 45 gallon polypropylene drums. The drums were then transported to the Water Research Laboratory at McMaster University for further processing. All equipment in contact with samples were scrupulously cleaned and rinsed with river water prior to the gathering of the actual sample.

2.2 Ozonation Apparatus and Procedure

Coagulated, settled and sand filtered Grand River water samples were ozonated in the ozonation apparatus, designed

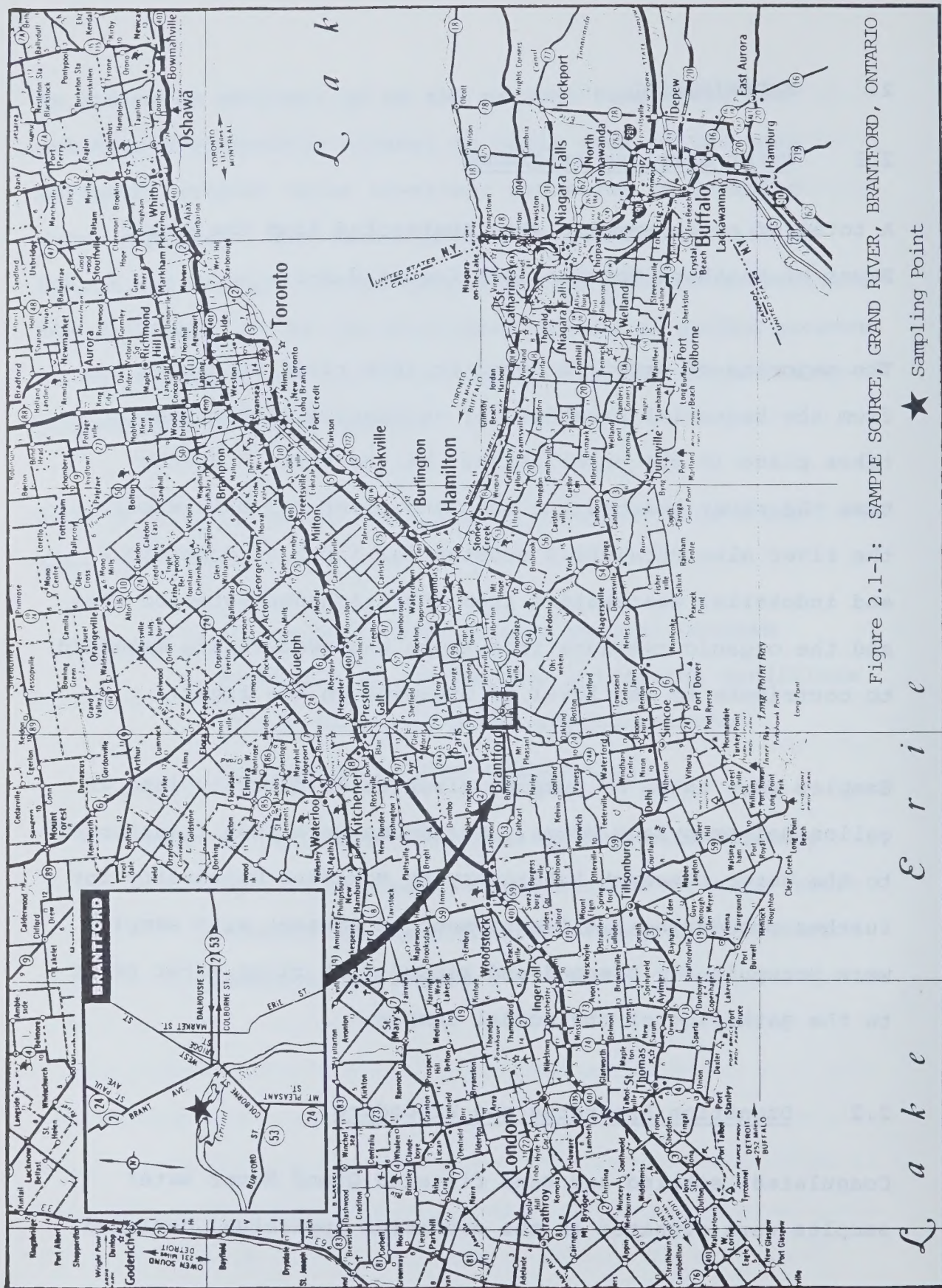


Figure 2.1-1: SAMPLE SOURCE, GRAND RIVER, BRANTFORD, ONTARIO

★ Sampling Point

and constructed at McMaster University, and this is shown schematically in Figure 2.2-1. The major components of the apparatus are a PSI ozone generator, a glass column 3 meters tall and 10 cm in diameter, a recirculating pump to simulate full-scale conditions, gas scrubbing bottles containing KI solution for ozone determinations, associated flow meters and flow control valves, and a heated tube to destroy waste ozone. Surfaces in contact with water or ozone are made of stainless steel, teflon or glass.

The ozone is introduced into the column through a porous glass bubbler. The ozone is transferred into water as the bubbles (≈ 1 mm in diameter, when at the bottom of the column) rise in the column. The ozone dissolution efficiency during the initial stages is nearly 100%, but this efficiency decreases at higher applied ozone dosages and as the ozone demand of the water diminishes.

The ozonation sequence starts with the transfer of a 24 litre sample of water into the column, using the recirculating pump. Subsequently, the setting of the bottom valve is changed such that the pump recirculates the water in the reactor for the entire run. Initially the ozone stream is directed to the feed ozone gas scrubbing bottles to measure the feed ozone concentration. This step is repeated after the ozonation run to obtain an average ozone concentration

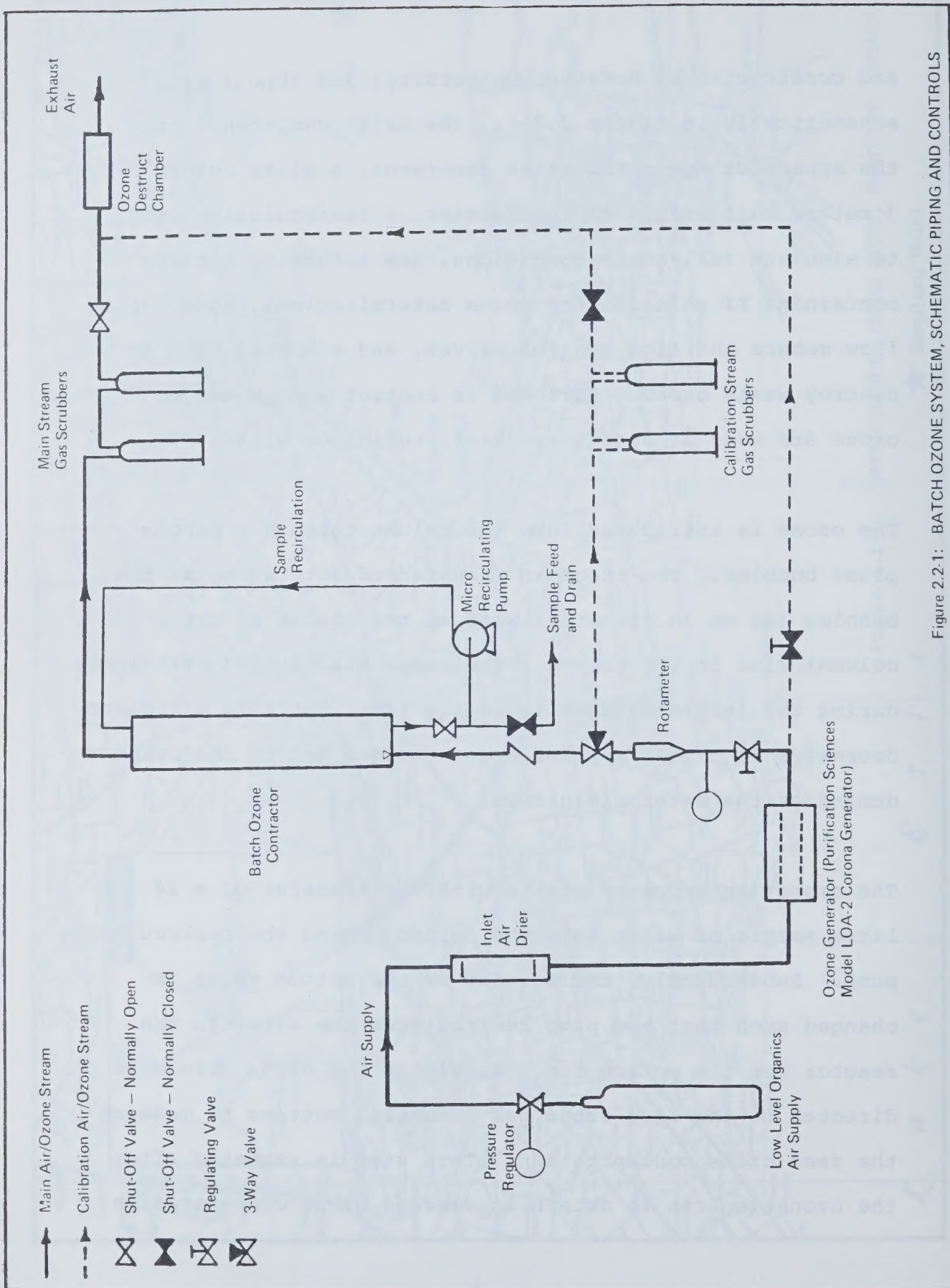


Figure 2.2-1: BATCH OZONE SYSTEM, SCHEMATIC PIPING AND CONTROLS

in the ozone feed stream.

The ozone then passes through the column for a period of time corresponding to the required applied ozone dosage (i.e. 3.5, 10.5, 20.0 and 30 min. for 2, 6, 12 and 20 mg of O_3 /l respectively).

The ozonated water is then drained from the column into a glass container and is allowed to stand for 24 hours prior to further treatment and analysis.

2.3 Biodegradation Apparatus and Procedure

Biodegradation studies were carried out in respirometers developed and constructed at McMaster University. The basic respirometer is shown schematically in Figure 2.3-1. Major components of the respirometer are the stirred reaction vessel, electrolytic cell, tube of KOH pellets to absorb the CO_2 produced by the biomass, and electronics to supply the constant current to produce the required oxygen and to integrate the current and time of operation.

The electrolytic cell is the center of the respirometer operation. As shown in Figure 2.3-1, the cell has an inner and outer section which are connected near the bottom to complete the electronic circuit to produce the oxygen, through the common electrolyte. The inner section, connected

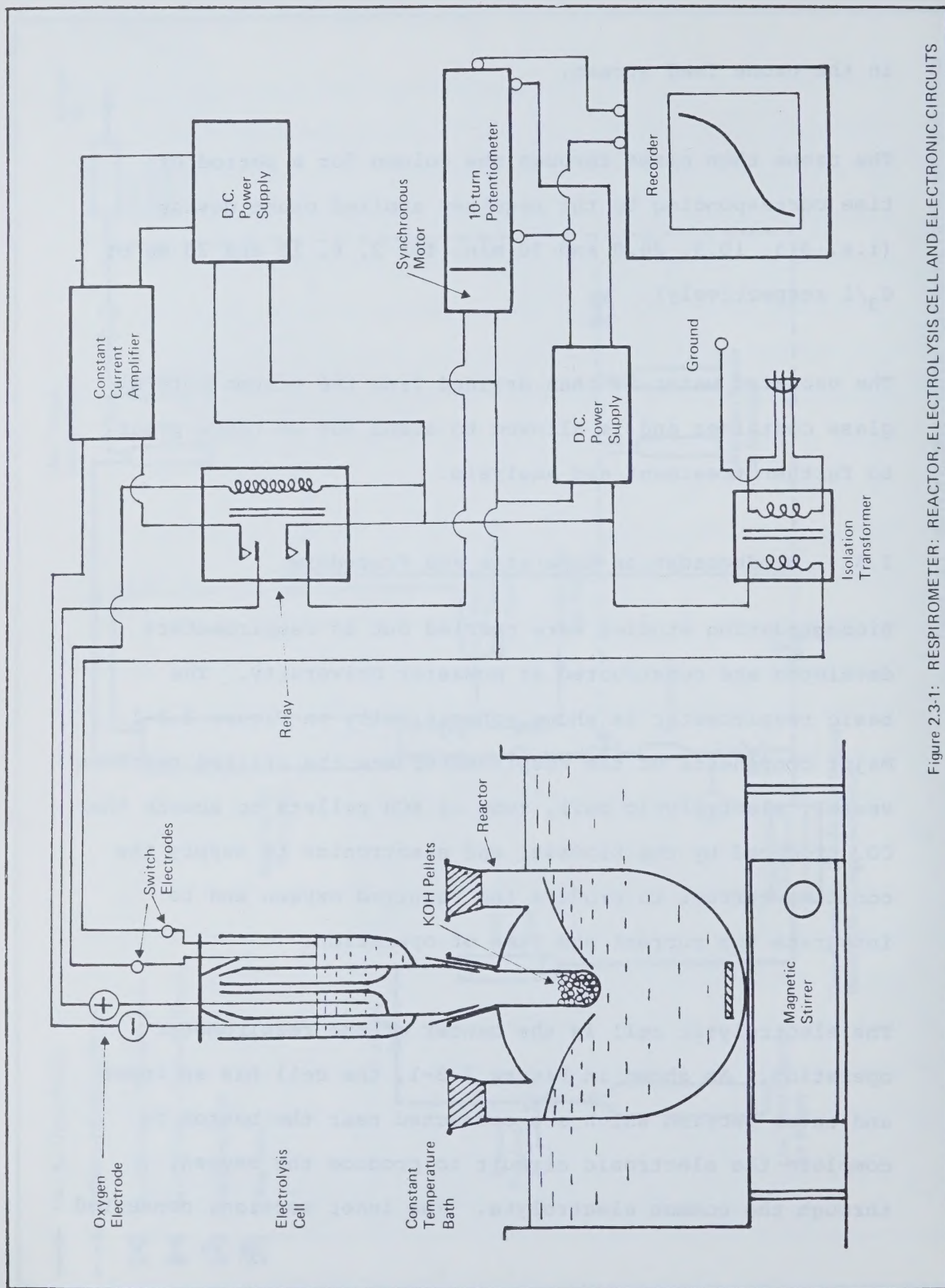


Figure 2.3-1: RESPIROMETER: REACTOR, ELECTROLYSIS CELL AND ELECTRONIC CIRCUITS

to the reactor through a high narrow tube, contains an electrode to produce oxygen. The outer section contains an electrode to produce the associated hydrogen and two additional electrodes that act as a switch.

When the cell is in balance the switch electrodes are immersed in the electrolyte thereby holding the electronics in the "OFF" position. When the oxygen is utilized by the biomass the pressure in the inner section of the cell drops (KOH absorbs the CO_2) and the electrolyte level rises while in the outer section the electrolyte level drops. Thus one of the switch electrodes is no longer immersed in the electrolyte, the electronic switching circuit is interrupted and the relays simultaneously turn on the current to produce oxygen and the uptake totalizing circuit. As the pressure in the inner section is re-established the switch electrodes again make contact and turn off the oxygen-producing current and the uptake totalizing circuit. The above operation is repeated as oxygen is required.

For this study, 10 litres of water and 100 ml biological seed (settled activated sludge) were placed in the reactors. A run lasted between 7 to 21 days. The plotted output of the respirometers are shown in Appendix C. The data shown in Appendix C is an average of two replicates run at each condition.

2.4 Adsorption Isotherm Apparatus and Procedure

Adsorption isotherms are used to determine the equilibrium loadings of solute on carbon.

For this study the activated carbon used was primarily Filtrasorb-400 (Calgon, Co., Pittsburgh, Pa.), although Hydrodarco 3000 (Atlas Chemicals, Brantford, Ont.) was also used. The carbons were crushed and sieved to 200 mesh. Amounts of carbon varying between 0 and 500 mg were added to 250 ml aliquots of water. Water-carbon suspensions were mixed continuously for 5 days using a tumbler mixer designed and constructed at McMaster University. The carbon was then separated from the water by filtration through 0.2 μ membrane. The filtrate was analyzed for TOC and UV absorbance.

The filter membranes chosen were Sartorius cellulose nitrate membranes as these filters contain the least amount of organic additives (as wetting agents aid). The filters were soaked in distilled water at least overnight. In addition 250 ml distilled water and 50 ml aliquot of water-carbon suspension intended for filtration were passed through each filter prior to collecting the sample used for analyses.

Adsorption of TOX and PAH were determined at one dosage of activated carbon in the isotherm studies.

The TOC data collected were used to calculate the set of points forming the adsorption isotherms.

2.5 Continuous Flow Adsorption Apparatus and Procedure

To study the effects of ozonated feed on carbon column performance, a parallel set of columns was set up as shown schematically in Figure 2.5-1. Coagulated, settled and sand filtered water was fed to one set of columns (each 2.5 cm i.d.) and the corresponding ozonated, coagulated, settled and sand filtered water was fed to the second set. The water was pumped through the columns by a duplex Masterflex variable speed pump (Cole-Palmer, Chicago, Illinois) at a rate of 10 ml/min, in a down flow mode. Each lead column contained 10.1 g activated carbon to a bed depth of 4.5 cm. The second columns contained 52.2 g activated carbon to a bed depth of 28 cm.

Daily samples were taken of the feed and of the effluent from each column. These samples were analyzed for TOC and UV absorbance.

Flowrates were monitored daily and adjusted as necessary.

For each batch of ozonated water, samples were taken for TOX analysis.

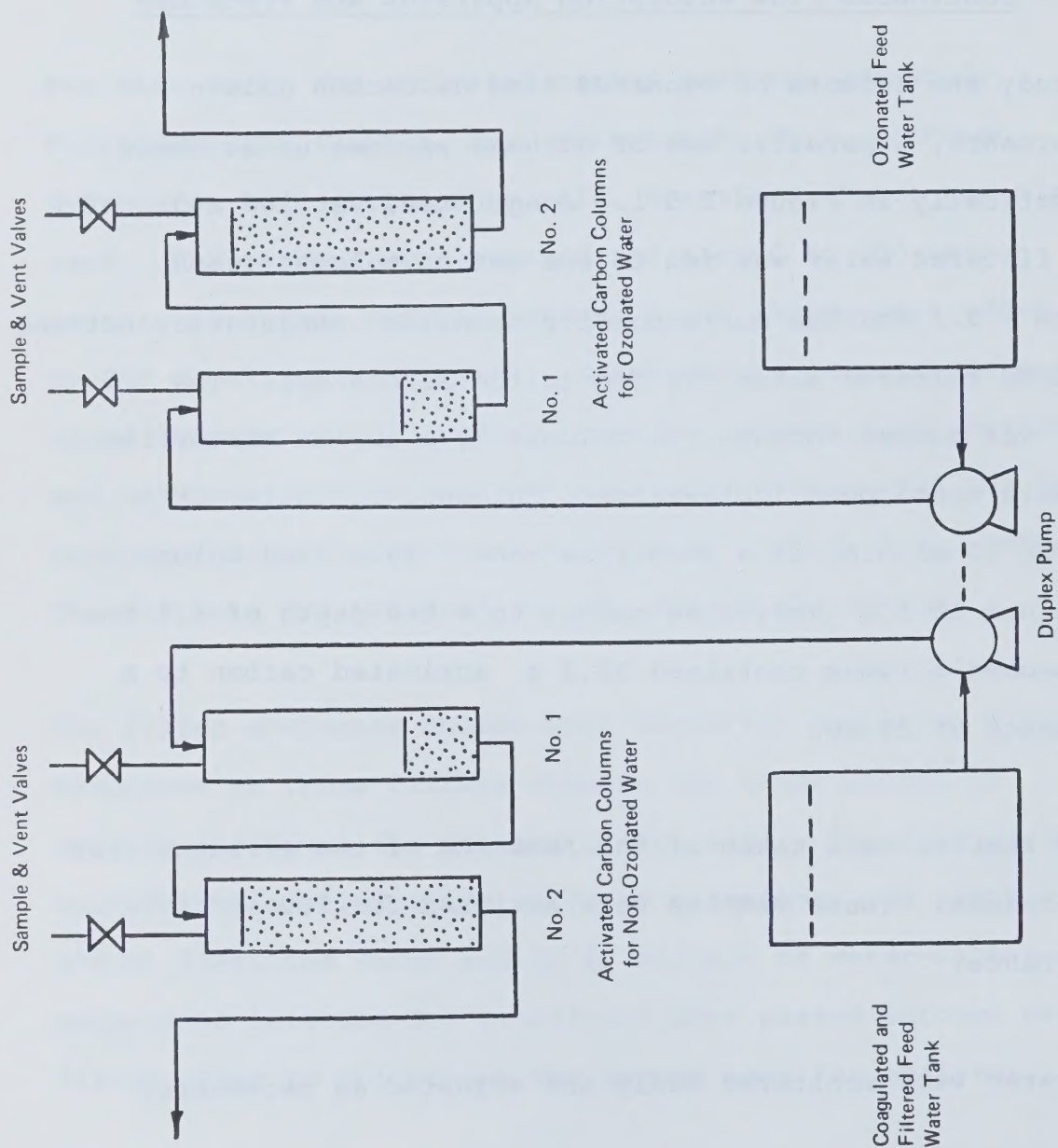


Figure 2.5-1: LABORATORY CONTINUOUS FLOW COLUMNS SCHEMATICS

Two sets of PAH analyses were done on final column effluents, during the initial period and during the final period of column operation.

2.6 Analytical Methods

A short summary of analytical methods is presented here; however a detailed description is provided in Appendix A.

Total Organic Carbon (TOC)

TOC levels were determined with the Dohrman DC-54 Ultra Low Level TOC Analyzer having a precision of $\pm 25 \mu\text{g/l}$ TOC.

UV Absorbance ($A_{254}^{10 \text{ cm}}$)

UV absorbance was determined with the Bausch and Lomb Spectronic 21 UV-D spectrophotometer using a 10 cm cell and a light wavelength 254 nm. The absorbance of the empty cell is set arbitrarily at 0.100 for instrument zero adjustment.

Chemical Oxygen Demand (COD)

COD analyses were carried out in accordance with EPA method (Storet No. 00335).

Total Organic Halide (TOX)

TOX was determined by sorbing organics from water on to XAD-2 resin and extracting with ether. The concentrated extract was then injected into the Dohrman MCTS-20 Microcoulometer for halide analysis in terms of Cl^- .

Polynuclear Aromatic Hydrocarbons (PAH)

The PAH were sorbed onto XAD-2 resin and extracted with ethyl ether. The concentrated extract was injected into a Varian Model 8500 HPLC connected to Varian 635 UV-VIS Spectrophotometer and Turner Model 111 Fluorometer.

Ozone

Ozone was determined according to Standard Method's (1975) iodometric method.

3. RAW WATER AND PRETREATED WATER CHARACTERISTICS

3.1 Raw Water Characteristics

The sample abstraction program was designed to cover late summer, winter, and spring run-off conditions. The sample numbers, dates of abstraction and major characteristics are summarized in Table 3.1-1.

The primary starting point for the study was pretreated water, i.e., alum coagulated, settled, and sand filtered water. Thus pretreated water analysis was essentially complete while raw water analysis was limited to pH and temperature measurements.

The pH of the raw water is essentially constant at 8.6, a value reasonably representative of carbonate-buffered natural water. The winter and spring melt (sample 7) temperature of this water is very near the freezing point, as expected.

Only occasional organic analyses were conducted on the raw water. These indicate a relatively high level of TOC, a low level of TOX (based on one sample) and a moderately high level of PAH. The nature of the PAH in these samples is shown in detail in Table 3.1-2.

TABLE 3.1-1 RAW WATER CHARACTERISTICS

Sample		Raw Water Characteristics									
No.	Date	pH	Temp. °C	TOC mg/l	COD mg/l	A ₂₅₄ 10 cm nm	TOX Filtered µg/l	TOX Suspended µg/l	ΣPAH Filtered ng/l	ΣPAH Suspended ng/l	
1	27/9/78	8.7	9.5	-	-	-	-	-	6.2	11.5	
2	18/10/78	8.6	9.5	-	-	-	-	-	35.1	10.2	
3	1/11/78	8.6	9.1	-	-	-	-	-	546	5180	
4	19/11/78	8.7	9.0	-	-	-	-	-	-	-	
5	8/ 1/79	8.6	0.5	10.3	-	1.930	-	-	-	-	
6	17/ 1/79	8.6	0.5	8.0	-	1.810	-	-	-	-	
7	5/3 /79	8.4	0.5	4.8	12.5	1.510	0.3	1.2	0.9	37.2	
Average		8.6	-	7.7	-	1.750	-	-	147.1	1309.7	
Standard Deviation ±		.1	-	2.2	-	.216	-	-	266.4	2580.2	

TABLE 3.1-2 DETAILS OF RAW WATER PAH CONCENTRATIONS

		Sample No.			
		1	2	3	7
Fluoranthene	Filtered	N.D.	12.0	100	N.D.
	Suspended	N.D.	4.6	1250	9.4
Pyrene	Filtered	1.7	3.7	24	.4
	Suspended	N.D.	3.7	333	5.7
Benzo (a) anthracene	Filtered	1.0	5.15	110	N.D.
	Suspended	5.25	.5	1177.4	3.7
Chrysene	Filtered	3.0	11.7	160	N.D.
	Suspended	3.0	1.3	1899	5.1
Perylene	Filtered	.52	1.89	43	.2
	Suspended	2.5	.05	227	3.1
Benzo (k) fluoranthene	Filtered	N.D.	.07	28	—
	Suspended	.07	.03	127	—
Benzo (a) pyrene	Filtered	.01	.56	1.5	.03
	Suspended	.05	.01	113	2.4
Dibenzo (a,h) anthracene	Filtered	—	—	5.6	.04
	Suspended	—	—	2	1.2
Benzo (g,h,i) perylene	Filtered	—	—	74	.2
	Suspended	—	—	50	6.7
TOTAL	Filtered	6.23	35.07	546.1	.9
	Suspended	11.25	10.19	5180	37.2

All units in ng/l.

N.D.: Not detected.

Typically, half or more of the PAH are attached to the suspended matter of the raw water. The concentration of PAH on suspended matter is particularly evident in the cases of samples 3 and 7. Sample 3, in particular, contained excessively high values of PAH; the origin of PAH in this sample has not been determined.

3.2 Pretreated Water Characteristics and the Effect of Pretreatment

The major characteristics of pretreated water are summarized in Table 3.2-1.

In general, pretreatment reduced the value of all parameters. The pH is reduced through alum addition while TOC, COD, $A_{254}^{10\text{ cm}}$, TOX and PAH levels are reduced by the removal of particulate organic matter by filtration and some dissolved organic matter by precipitation. Fractional removals can be tabulated meaningfully for only two parameters, TOC and PAH, as shown in Table 3.2-2.

The percent removal of TOC is consistently around 37 percent by pretreatment. This level of organic removal is typical of North American water treatment plants which, with the addition of chlorine, commonly use the pretreatment scheme of the present experiments as their complete water renovation method. On the other hand, in the case of the Seine, which

TABLE 3.2-1 PRE-TREATED WATER CHARACTERISTICS

Sample No.	Date	pH -	TOC mg/l	COD mg/l	A ₂₅₄ nm 10 cm -	TOX µg/l	ΣPAH ng/l
1	27/ 9/78	8.4	6.2	11.5	1.246		10.13
2	18/10/78	8.3	5.5	10.7	1.146		2.8
3	1/11/78	8.3	5.6	11.7	1.000	6	61.9
4	19/11/78	8.4	3.7	10.7	1.083	2	4.06
5	8/ 1/79	8.4	6.7	12.7	1.860	2	
6	17/ 1/79	8.3	4.6	10.2	1.224	3.5	72.5
7	5/ 3/79	8.3	3.2	7.3	.894	ND	
Average		8.3	5.1	10.7	1.208	2.7	30.3
Standard Deviation ±		.05	1.3	1.7	.313	2.2	34.0

has similar raw water qualities to that of the Grand River, French water treatment plants often accomplish better than 50% organic removal with the aid of relatively high alum dosage and solid contact clarification (Benedek and Bancsi, 1977).

TABLE 3.2-2 THE REMOVAL OF TOC AND Σ PAH AS A RESULT OF PRETREATMENT (Expressed as Percent Removal on the Basis of Raw Water Values).

Sample No.	Percent Removal	
	TOC	Σ PAH
1	-	43
2	-	94
3	-	99
4	-	-
5	35	-
6	42	-
7	35	-
Average	37	79
Standard Deviation $\pm$	4	31

Interestingly, the PAH removal values vary greatly due to the fact that regardless of raw water quality, the pre-treated PAH levels are reduced below 70 ng/l. Thus the pretreatment system is relatively effective in reducing the strongly fluctuating PAH values of the raw water. The individual PAH concentrations are shown in Table 3.2-3. It is interesting to note that the PAH levels remaining after

TABLE 3.2-3 DETAILS PRETREATED WATER PAH CONCENTRATIONS

	Sample No.				
	1	2	3	4	7
Fluoranthene	N.D.	1.7	24.4	N.D.	18.3
Pyrene	2.7	.2	15.3	N.D.	8.1
Benzo (a) anthracene	2.9	.05	8.6	2	17.3
Chrysene	4.0	.4	6.5	1.2	24.6
Perylene	.32	.29	1.8	.3	1.5
Benzo (k) fluoranthene	.09	.1	.4	.08	—
Benzo (a) pyrene	.12	.06	.5	.12	.4
Dibenzo (a,h) anthracene	—	—	1.5	.09	1.0
Benzo (g,h,i) perylene	—	—	2.7	.27	1.2
TOTAL	10.13	2.8	61.7	4.06	72.5

All units in ng/l.

N.D. is not detected.

pretreatment are drastically lower than those found in raw water.

The pretreated values for TOX are also relatively low with the exception of sample 1, however, the TOX procedure was not yet standardized during this period of analysis.

Unfortunately, only one set of raw water TOX values were obtained hence the effect of pretreatment on halogenated organics can not be determined. In general, it is probable that the level of halogenated organics in the raw water are relatively low and that pretreatment (in the absence of chlorination) reduces these to consistent levels.

It is postulated that the relatively low TOC levels are probably due to significant run-off input, i.e. non-point rather than point pollution sources. It is further postulated, on the basis of the above data, that the low COD-to-TOC ratios are a reflection of such non-point sources. In general, it appears that the levels of organics do not follow clear seasonal variations except for the fact that the snow-melt sample (No. 7), contained the lowest (most diluted) level of TOC.

The ratio of average COD to TOC is 2.18 as shown in Table 3.2-4. Such a low value normally indicates highly oxidized organics, more specifically, organic compounds containing more oxygen than the stoichiometric amount

TABLE 3.2-4 THE RATIOS OF COD:TOC FOR PRETREATED WATER

Sample No.	TOC (mg/l)	$\frac{\text{COD}}{\text{TOC}}$
1	6.2	1.87
2	5.5	1.95
3	5.6	2.07
4	3.1	2.93
5	6.7	1.90
6	4.6	2.20
7	3.2	2.31
Average	5.1	2.18
Standard Deviation $\pm$	1.3	0.40

required for the oxidation of the hydrogen contained in the compound to water [e.g., the COD:TOC ratio is 2.67 for glucose (a stoichiometrically balanced hydrogen/oxygen compound) and 1.33 for formic acid (a highly oxidized compound)]. Organics in river water are usually considered to be in a highly oxidized state, although a value of 2.18 is low enough to assume that some incomplete oxidation of some of the organics in the COD test may also occur.

As shown in Table 3.2-4, the COD-to-TOC ratios vary from 2.93 (sample 4, late fall) to 1.87 (sample 1, Indian summer).

This variation indicates that the nature of the organics fluctuates between samples and is probably influenced by man's activities. Furthermore, a careful examination of the variation of the COD-to-TOC ratio with TOC level indicates that the ratio increases with decreasing levels of TOC. This may indicate that the organics originating from human activities tend to break down to a more highly oxidized state (or that they are not oxidized in the COD test) than the complex humic and fulvic materials that form the background "natural" TOC of the river water.

4. OZONATION STUDIES

4.1 TOC Removal

Figure 4.1-1 shows the removal of TOC as a function of time. In general, TOC removal was linear with respect to ozonation time on the semi-log scale used in Figure 4.1-1, and this indicates that TOC removal is first order with respect to a given aqueous ozone level (assuming "pseudo" steady-state is reached in the experimental contactor). Thus one can postulate that

$$\frac{d \text{TOC}_O}{dt} = K \text{TOC}_O \quad (4.1-1)$$

where TOC_O = TOC level at anytime, t , during ozonation

K = constant (a function of aqueous ozone level)

Sample 7 appears to have two different straight line regions. This may indicate the presence of two significantly different types of organic compounds possibly arising from the substantial input of snow-melt to the river during the sampling period.

The value(s) of K for each sample can be determined directly from Figure 4.1-1, and Table 4.1-1 lists the calculated values. The values fall into two categories, samples 1, 2, 4, and 7 (second coefficient) are all similar and relatively low

Figure 4.1-1: TOC REMOVALS AS A FUNCTION OF OZONATION TIME

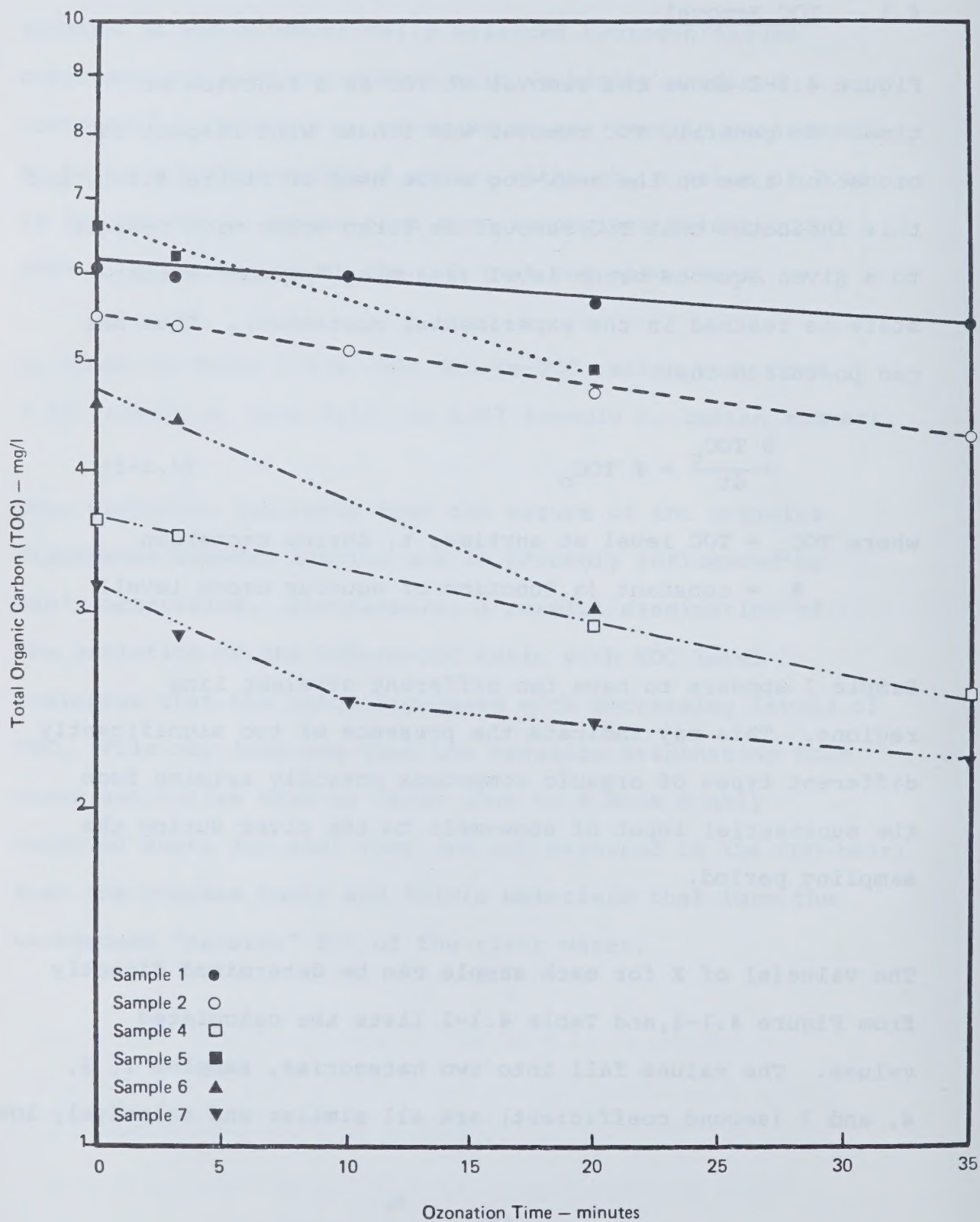


TABLE 4.1-1 FIRST ORDER REACTION RATE CONSTANTS (K)
FOR TOC REMOVAL

Sample	K (min ⁻¹)
1	0.0041
2	0.0073
3	-
4	0.0108
5	0.0155
6	0.0221
7 (first part)	0.0233
(second part)	0.0048

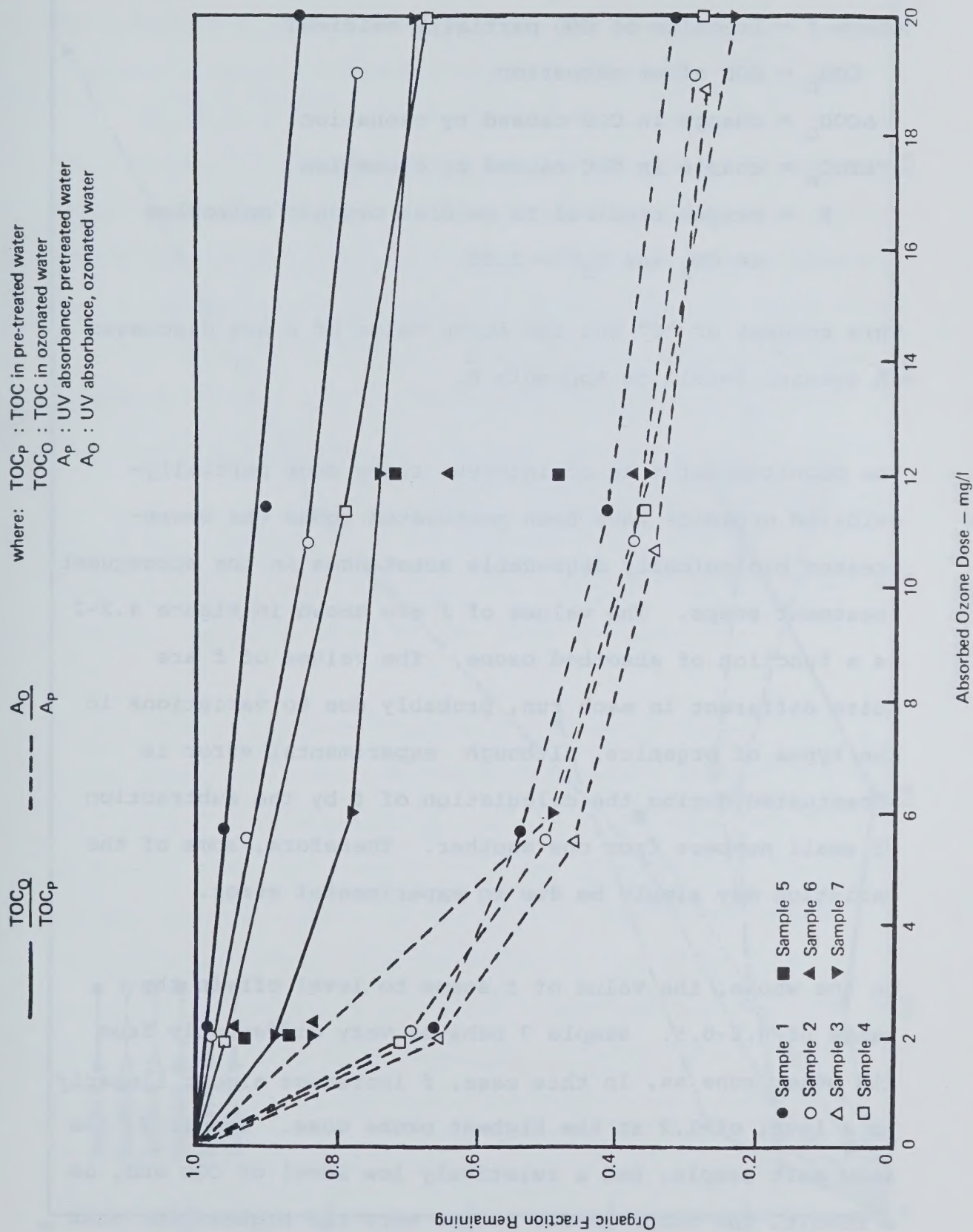
in magnitude whereas samples 5, 6 and 7 (first coefficient) are similar and more than twice as high as the first group. If sample 7 is discounted, the observed grouping seems to be primarily a function of season, however, the mechanistic reasons behind this variation in TOC removal by ozonation are not clear.

4.2 Selectivity in Organic Removal and Partial Oxidation

Figure 4.2-1 displays the decrease of TOC and UV absorption with increased ozone dose. These curves clearly shows that the reduction in $A_{254 \text{ nm}}^{10 \text{ cm}}$ absorption is much greater than that in TOC. Since the ultraviolet light absorption at 254 nm is primarily by unsaturated organic molecules, increased reduction in $A_{254 \text{ nm}}^{10 \text{ cm}}$ indicates either preferential oxidation of unsaturated compounds or incomplete oxidation of the remaining oxidized fragments, or a combination of both. Some incomplete oxidation should be anticipated and therefore an attempt was made to estimate the partially oxidized fraction by comparing reductions in the level of TOC and COD. This comparison is based on the fact that changes in COD indicate the total amount of oxidation whereas TOC changes only indicate complete oxidation to CO_2 . Thus we can define a fraction, f , as follows:

$$f = \frac{\Delta \text{COD}_o - X \Delta \text{TOC}_o}{\text{COD}_o} \quad (4.2-1)$$

Figure 4.2-1: DIFFERENCES BETWEEN TOC AND UV REMOVALS AS A FUNCTION OF OZONE DOSE



where f = fraction of COD partially oxidized

COD_O = COD after ozonation

ΔCOD_O = change in COD caused by ozonation

ΔTOC_O = change in TOC caused by ozonation

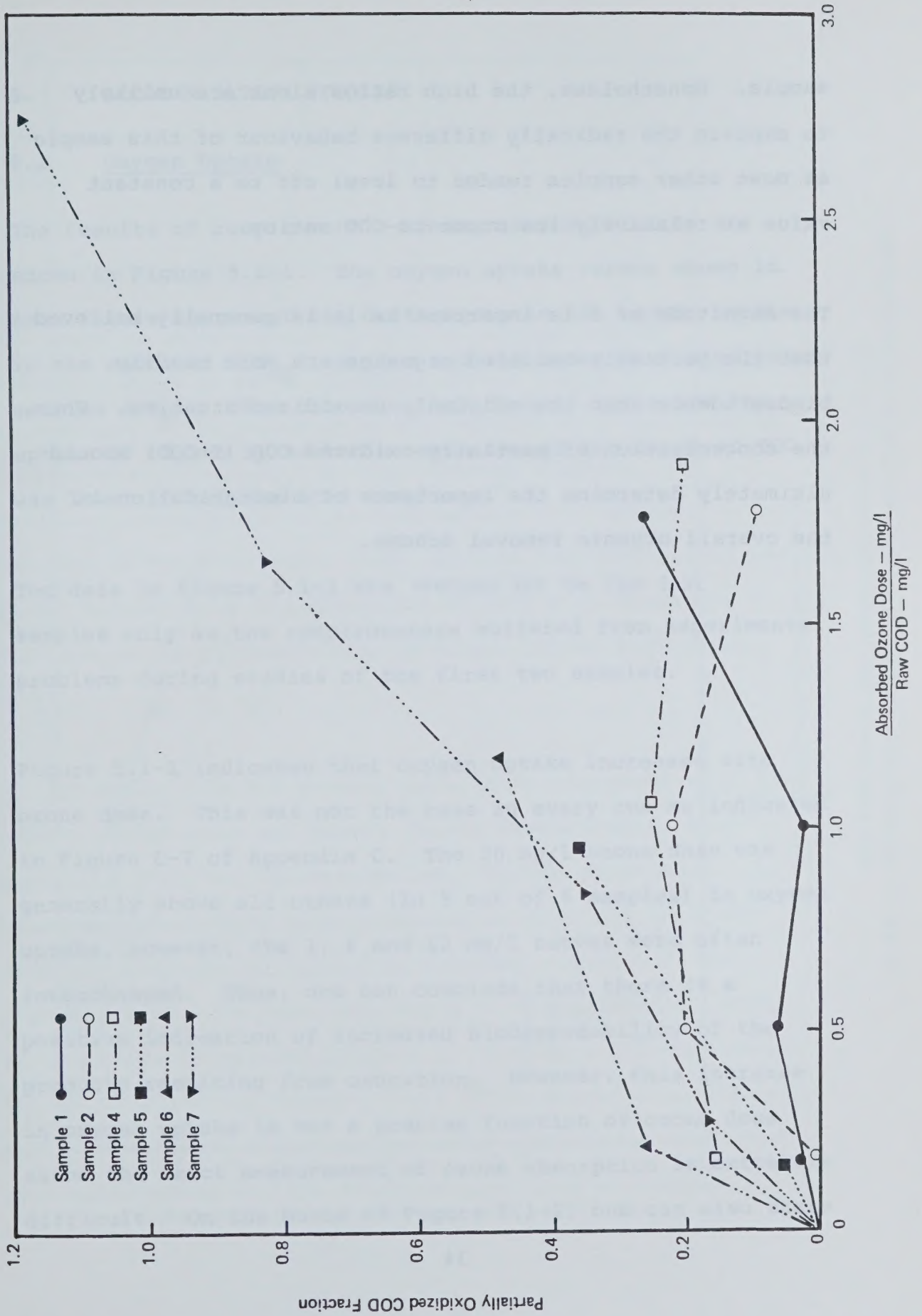
X = oxygen required to oxidize organic molecules
to CO_2 and H_2O = 2.62

This concept of " f " and the above value of X are discussed in greater detail in Appendix E.

The magnitude of f is of interest since such partially-oxidized organics have been postulated to be the ozone-created biologically degradable substances in the subsequent treatment steps. The values of f are shown in Figure 4.2-2 as a function of absorbed ozone. The values of f are quite different in each run, probably due to variations in the types of organics, although experimental error is accentuated during the calculation of f by the subtraction of small numbers from one another. Therefore, some of the variation may simply be due to experimental error.

On the whole, the value of f seems to level off in the range of 0.2-0.5. Sample 7 behaves very differently from all other runs as, in this case, f increases almost linearly to a level of 1.2 at the highest ozone dose. Sample 7, the snow melt sample, had a relatively low level of COD and, as a result, the ozone-to-COD ratios were the highest for this

Figure 4.2-2: LEVELS OF PARTIALLY OXIDIZED ORGANICS (COD) AT DIFFERENT OZONE: COD RATIOS



sample. Nonetheless, the high ratios alone are unlikely to explain the radically different behaviour of this sample as most other samples tended to level off to a constant value at relatively low ozone-to-COD ratios.

The magnitude of f is important as it is generally believed that the partially-oxidized organics are more readily biodegradable than the original, unoxidized organics. Thus, the concentration of partially-oxidized COD (f COD) should ultimately determine the importance of biodegradation in the overall organic removal scheme.

5. BIODEGRADATION STUDIES

5.1 Oxygen Uptake

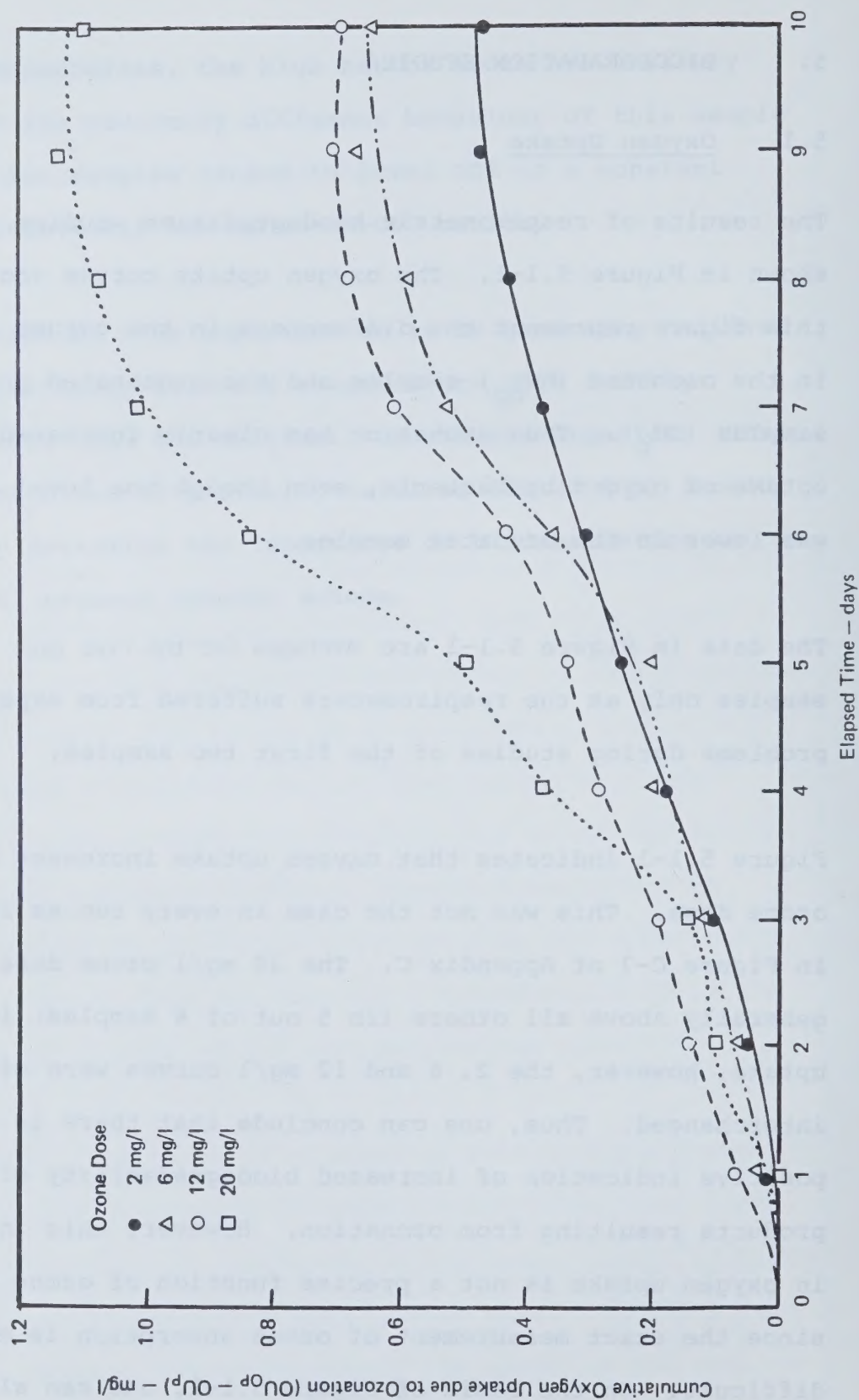
The results of respirometric biodegradation studies are shown in Figure 5.1-1. The oxygen uptake curves shown in this figure represent the differences in the oxygen uptake in the ozonated (OU_{op}) samples and the unozonated pretreated samples (OU_p). Thus ozonation has clearly increased the uptake of oxygen by bacteria, even though the level of TOC was lower in the ozonated samples.

The data in Figure 5.1-1 are averaged for the five last samples only as the respirometers suffered from experimental problems during studies of the first two samples.

Figure 5.1-1 indicates that oxygen uptake increases with ozone dose. This was not the case in every run as indicated in Figure C-7 of Appendix C. The 20 mg/l ozone dose was generally above all others (in 5 out of 6 samples) in oxygen uptake, however, the 2, 6 and 12 mg/l curves were often interchanged. Thus, one can conclude that there is a positive indication of increased biodegradability of the products resulting from ozonation. However, this increase in oxygen uptake is not a precise function of ozone dose since the exact measurement of ozone absorption is extremely difficult. On the basis of Figure 5.1-1, one can also state

Figure 5.1-1: RELATIVE ENHANCEMENT OF AVERAGE RESPIROMETRIC OXYGEN UPTAKE
AS A FUNCTION OF TIME (Average of Samples Nos. 3, 4, 5, 6 & 7)

OU_{OP} : Oxygen uptake of pretreated and ozonated samples
 OU_P : Oxygen uptake of pretreated only samples



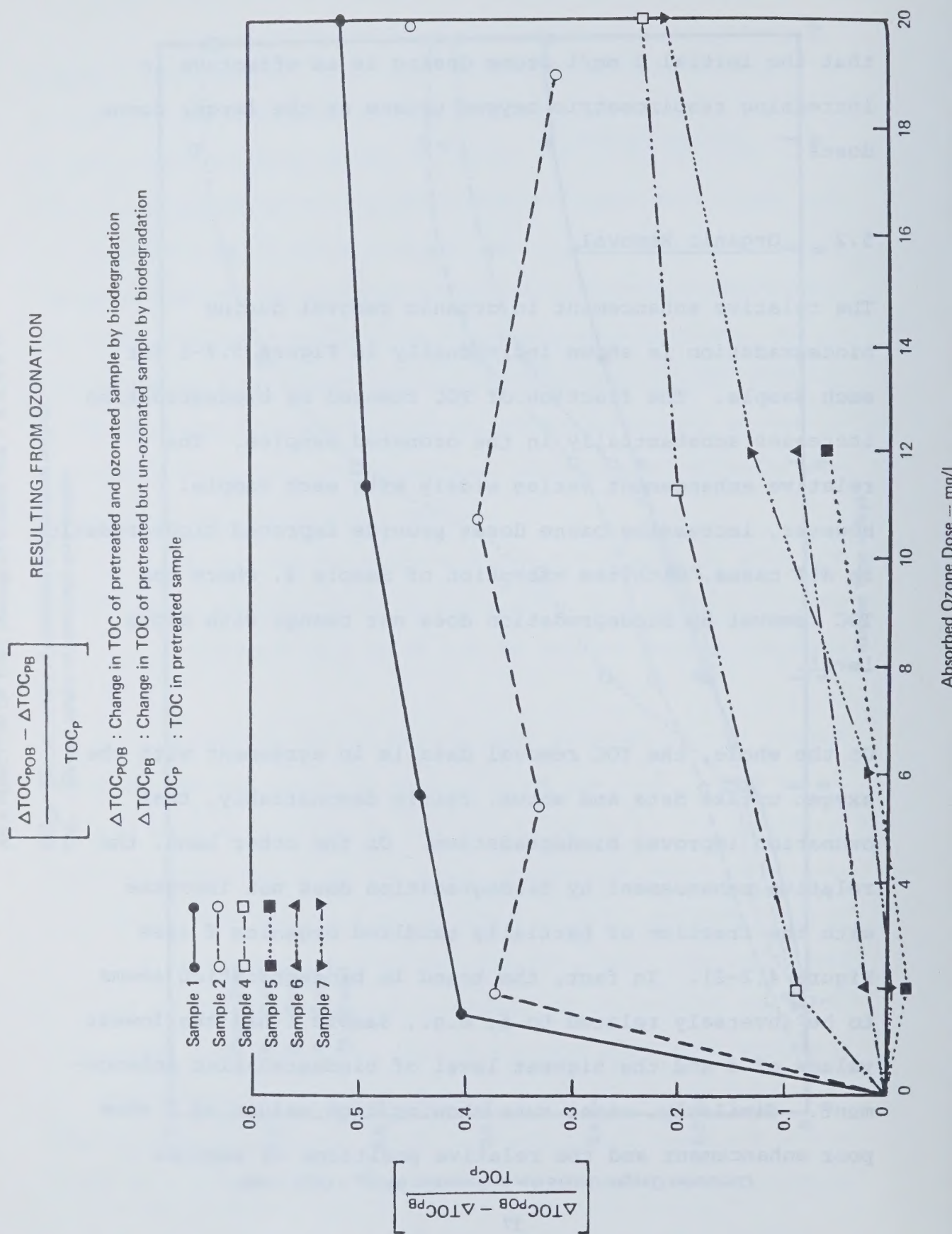
that the initial 2 mg/l ozone dosing is as effective in increasing respirometric oxygen uptake as the larger ozone doses.

5.2 Organic Removal

The relative enhancement in organic removal during biodegradation is shown individually in Figure 5.2-1 for each sample. The fraction of TOC removed by biodegradation increases substantially in the ozonated samples. The relative enhancement varies widely with each sample. However, increasing ozone doses provide improved biodegradation in all cases, with the exception of Sample 2, where the TOC removal by biodegradation does not change with ozone level.

On the whole, the TOC removal data is in agreement with the oxygen uptake data and shows, fairly demonstrably, that ozonation improves biodegradation. On the other hand, the relative enhancement by biodegradation does not increase with the fraction of partially oxidized organics f (see Figure 4.2-2). In fact, the trend in biodegradation seems to be inversely related to f , e.g., Sample 1 had the lowest values of f and the highest level of biodegradation enhancement. Similarly, other runs showing high values of f show poor enhancement and the relative positions of samples

Figure 5.2-1: THE RELATIVE ENHANCEMENT IN ORGANICS BIODEGRADATION



are inversed between Figures 4.2-2 and 5.2-1. The reason for this behaviour is not clear.

On the basis of a more detailed consideration, this trend appears to be contrary to the general trend observed for organics degradation. Thus the results may simply be due to experimental error which is enhanced during the use of equation 4.2-1. It is also probable that, at higher doses of ozone, the impurities like heavy paraffin oils present in the filtered water tend to accumulate in the reaction system. These relatively refractory impurities are not likely to be degraded fast enough to show an increase in oxygen uptake.

In all probability, there is an optimum ozone dose for any system. An initial small amount of ozone may initiate sites for microbiological attack but, as ozonation proceeds, the molecules may again become refractory in the case of humic and fulvic materials which constitute most of the organics in surface waters.

According to M. Malaiyandi (Private Communication), "In the ozonation studies on polycyclic aromatic systems, the major degradation products, apart from carbon dioxide, are oxalic acid and other dicarboxylic acids. Oxalic acid

offers considerable resistance to ozone oxidation and its accumulation renders itself refractory to microbial degradation. A further study is necessary to assess the effect of ozonation on low molecular weight dicarboxylic acids."

It would appear, from all of the above, that between 6 and 12 mg/l ozone concentration or dose is most appropriate for the degradation of some of the more refractory organics in water.

6. ACTIVATED CARBON ADSORPTION

6.1 Adsorption Isotherm Studies

Adsorption isotherms are discussed in detail by Benedek (1974). Briefly, isotherms represent equilibrium organic loadings on activated carbon resulting from contact between the activated carbon and the organics contained in the water being treated. The set of points forming the isotherm plot is calculated in accordance with the following relationship:

$$q = \frac{V(C_o - C_e)}{m} \quad (6.1-1)$$

where:

q = equilibrium carbon loading, mg TOC/g AC

V = aliquot, volumetric, of water treated, litres

C_o = organic concentration in the water before
carbon contact, mg TOC/l

C_e = organic concentration in the water after
carbon contact, mg TOC/l

m = mass of activated carbon used to contact
water, grams

The adsorption isotherm is obtained by plotting " q " versus " C_e " and represents the equilibrium distribution between the activated carbon and water phases. The plot representing the adsorption of a single organic material or of a mixture

of essentially similar organic materials will generally exhibit linearity. Mixtures of significantly different organic materials could result in plots which are to some extent curvilinear, generally levelling off to the right.

The two most important interpretive points on an adsorption isotherm are the capacity, q , observed at the actual feed concentration, and the concentration, C_e , observed at zero q . The first observation represents the maximum expected capacity (mg TOC/g AC) in granular carbon systems while the second refers to the highest obtainable treatment (TOC removal) level.

Two sets of adsorption isotherms are presented in Appendix D. The first set of three isotherms, shown in Figure D-1, D-3 and D-12, are those obtained from Samples 1, 2 and 7 respectively immediately after ozonation at different ozone doses, including the zero ozone dose or pretreated-only sample. The second set consists of ten figures. Figures D-2, D-4, D-5, D-9, D-10, D-11 and D-13 show the isotherms obtained from Samples 1 to 7 respectively after biodegradation and when using Filtrasorb-400 activated carbon. Figures D-6, D-7 and D-8 are comparative isotherms for two activated carbons, Filtrasorb-400 and Hydrodarco-3000, used to treat Sample 3 after biodegradation and ozonation at various ozone doses.

The isotherm data for individual samples is difficult to interpret as trends vary from sample to sample. Accordingly, composite isotherms are developed by putting the data for all seven samples at a given treatment on a single graph and drawing the line of best fit using the method of least squares. These are shown in Figures D-14 to D-17 inclusive.

Prior to biodegradation, the scatter in the data is very significant and, as shown in Figure 6.1-1, the confidence limits are very wide. After biodegradation, the confidence intervals narrow, as shown in Figure 6.1-2. The least squares lines obtained from data for ozonated and pretreated water are shown in Figure 6.1-3. On the basis of this figure, ozonation appears to result in an initial increase in adsorptivity, at 2 mg/l ozone dose, but a decrease in adsorptivity as the ozonation dose increases.

In view of the confidence intervals noted earlier, as well as hypothesis testing, the above trends are statistically insignificant and, in general, the effect of ozonation on adsorptivity appears to be insignificant. Other investigators (Benedek 1977, Kuhn et al, 1978) indicate that ozonation should decrease adsorptivity in the above studies, however, this conclusion is based on a single set of isotherms and, at least in one case, (Benedek, 1977), analytical equipment

Figure 6.1-1: COMPOSITE ACTIVATED CARBON ADSORPTION ISOTHERM
(LEAST SQUARES FITTED), SHOWING 95% CONFIDENCE LIMITS

Pretreated and Ozonated Samples

Ozone Dose: 2 mg/l

Mean C_0 : 4.507 mg/l

Standard Deviation: 1.578 for C_0

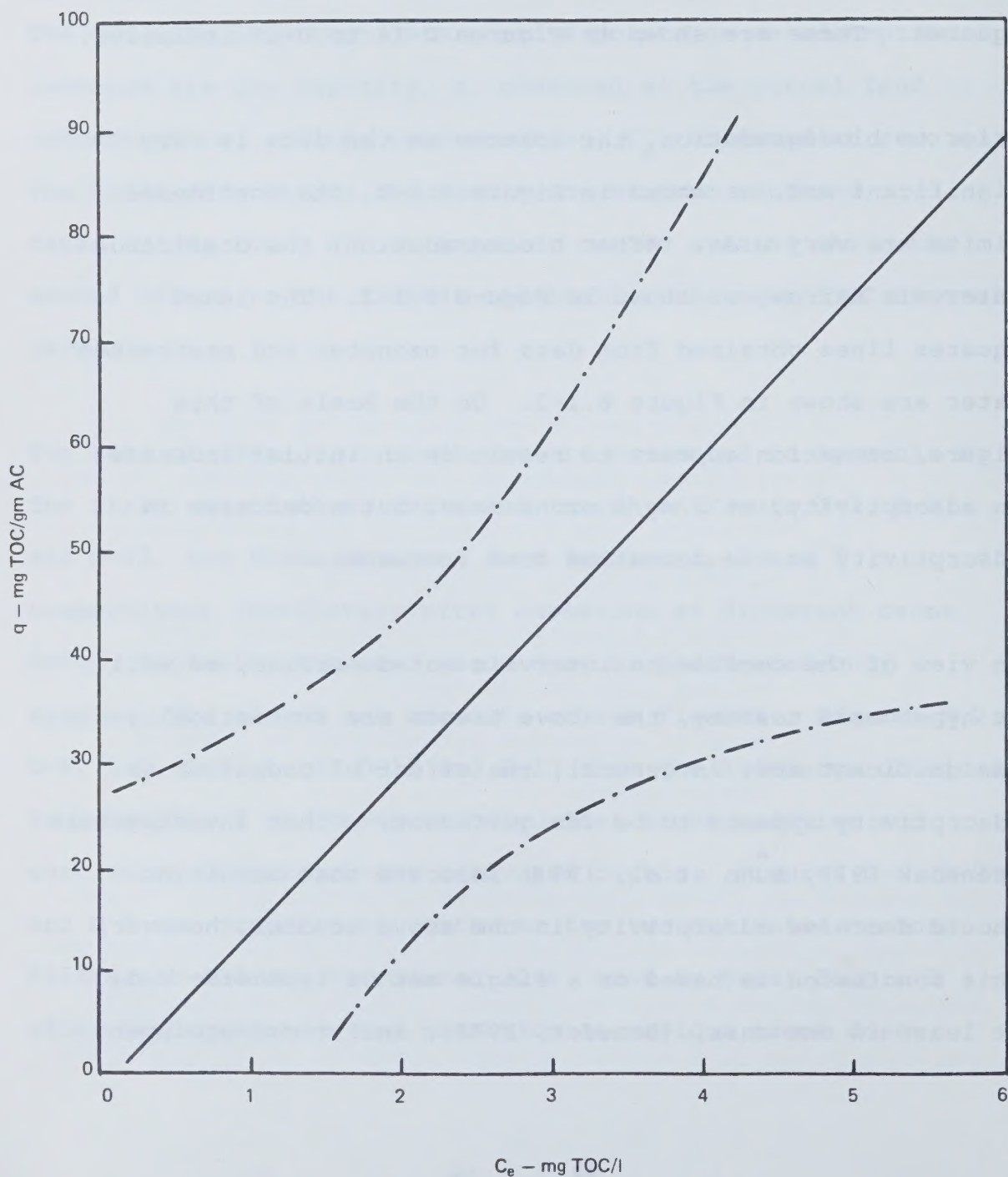


Figure 6.1-2: COMPOSITE ACTIVATED CARBON ADSORPTION ISOTHERM
(LEAST SQUARES FITTED), SHOWING 95% CONFIDENCE LIMITS

Pretreated, Ozonated and Biodegraded Samples

Ozone Dose: 2 mg/l

Mean C_o : 3.830 mg/l

Standard Deviation: 1.232 for C_o

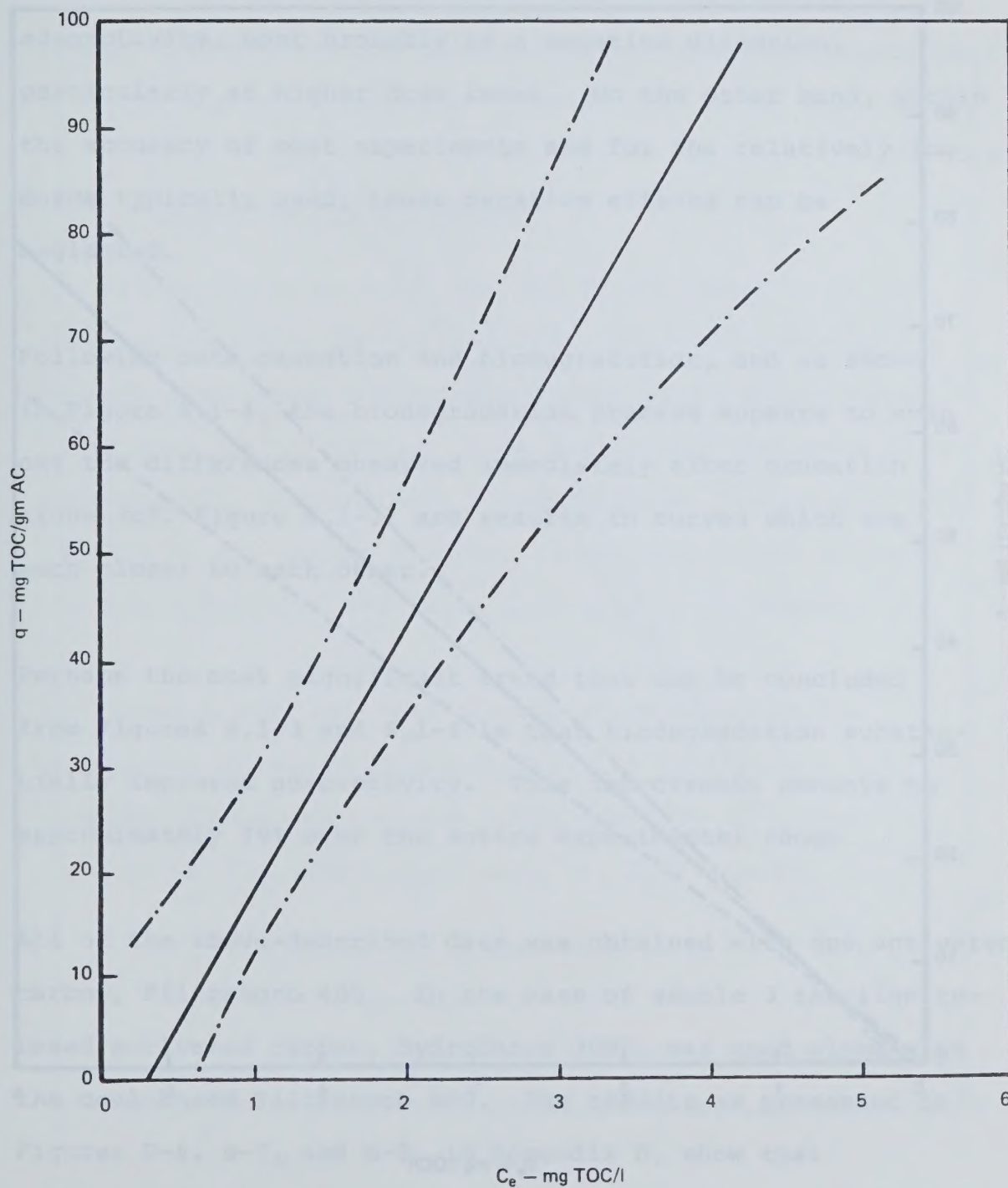


Figure 6.1-3: COMPOSITE ACTIVATED CARBON ADSORPTION ISOTHERM
(LEAST SQUARES FITTED)

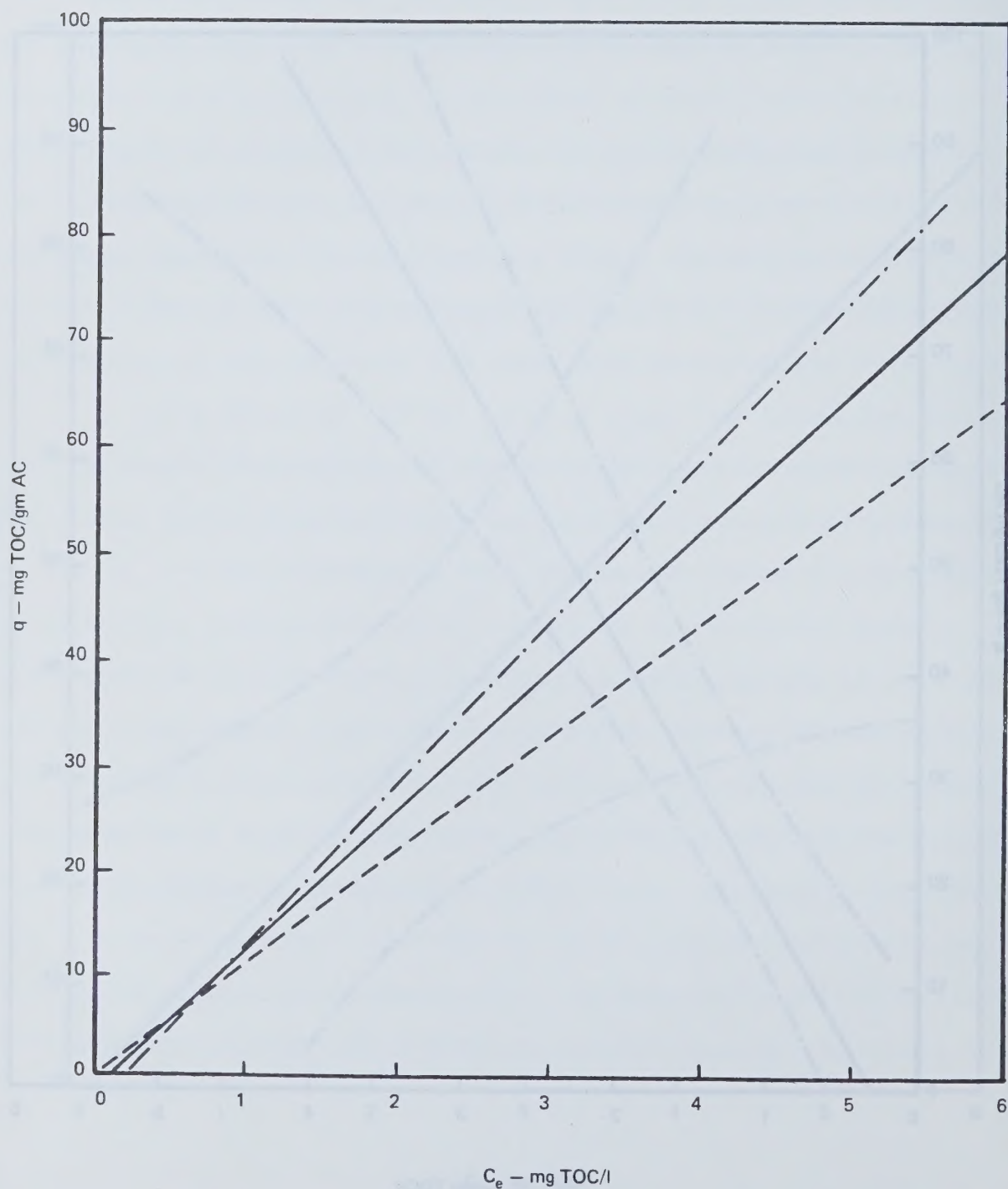
Post-Ozonation

Ozone Dose (mg/l)

Mean C_o

Standard Deviation for C_o

—	0	4.586	1.556
- · - · -	2	4.507	1.578
- - -	12	3.894	1.763



was inferior to that used in this study. In the present study, on the basis of a single isotherm, we could have concluded that ozonation decreases or increases adsorptivity. On the basis of series of isotherms, the conclusions are that, in terms of TOC, ozonation only weakly affects adsorptivity, most probably in a negative direction, particularly at higher dose level. On the other hand, within the accuracy of most experiments and for the relatively low doses typically used, these negative effects can be neglected.

Following both ozonation and biodegradation, and as shown in Figure 6.1-4, the biodegradation process appears to even out the differences observed immediately after ozonation alone (cf. Figure 6.1-3) and results in curves which are much closer to each other.

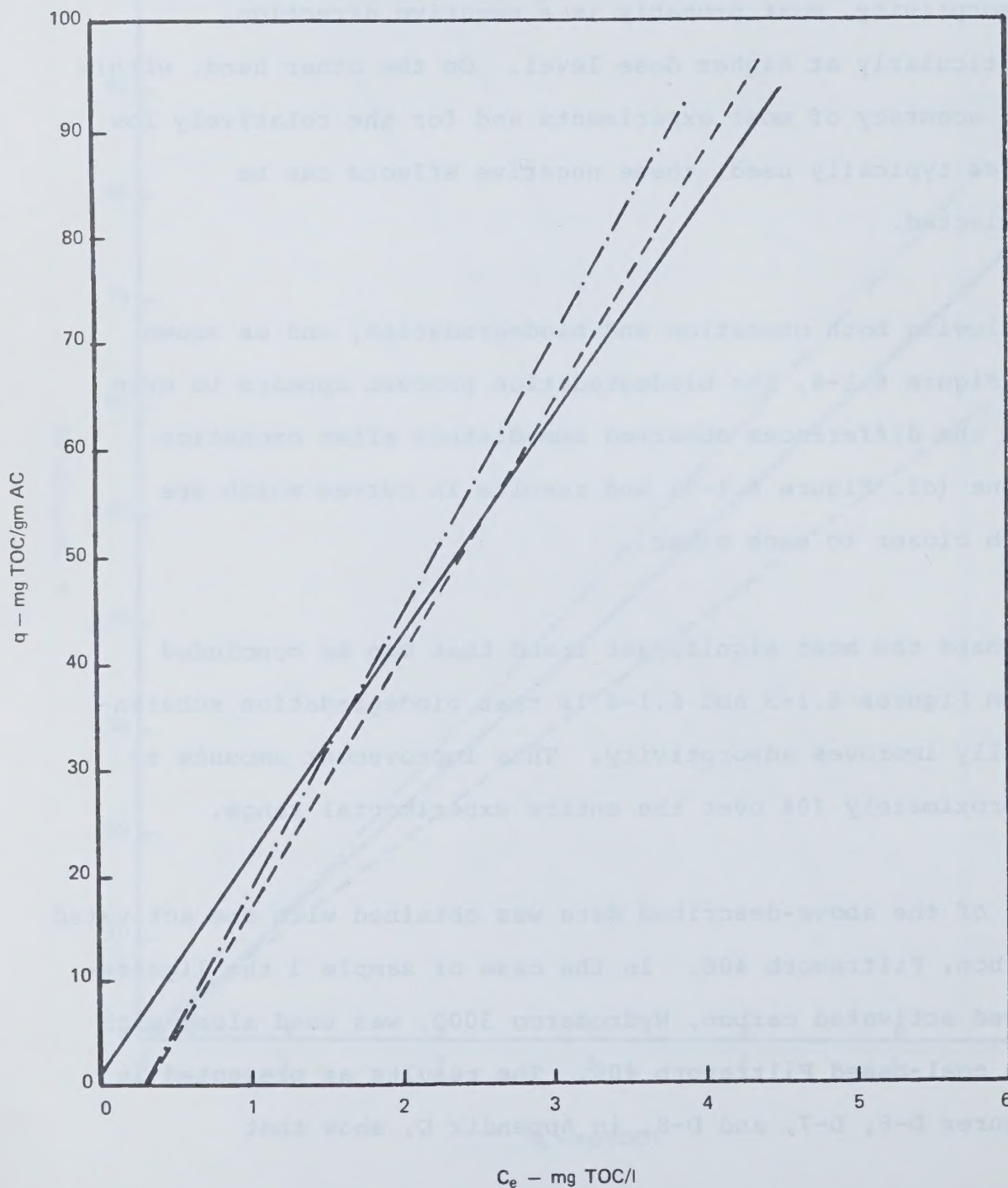
Perhaps the most significant trend that can be concluded from Figures 6.1-3 and 6.1-4 is that biodegradation substantially improves adsorptivity. This improvement amounts to approximately 70% over the entire experimental range.

All of the above-described data was obtained with one activated carbon, Filtrasorb 400. In the case of sample 3 the lignite-based activated carbon, Hydrodarco 3000, was used along with the coal-based Filtrasorb 400. The results as presented in Figures D-6, D-7, and D-8, in Appendix D, show that

Figure 6.1-4: COMPOSITE ACTIVATED CARBON ADSORPTION ISOTHERM
(LEAST SQUARE FITTED)

Post-Ozonation and Respirometry

Ozone Dose (mg/l)	Mean C_0	Standard Deviation for C_0
0	4.143	1.156
2	3.830	1.232
12	2.511	0.738



Filtrisorb 400 was superior to Hydrodarco under the conditions shown in the above figures. At all three stages of isotherm study (i.e. after pre-treatment, ozonation and biodegradation), Filtrasorb 400 adsorbed more than twice as much TOC as Hydrodarco 3000. These results are in essential agreement with the results of Benedek and Bancsi (1977) who found that Filtrasorb 400 was superior to Hydrodarco 3000 in removing organics from water supplies.

6.2 Continuous Flow Studies

The breakthrough patterns for the first, short (4.5 cm) columns are shown in Figure 6.2-1. Both the ozonated and non-ozonated water-fed columns showed rapid breakthrough in TOC rising to 0.8 C/Co at 70 mg applied TOC per gram of AC. Subsequently, the effluent concentrations fluctuate between the 0.8 to 1.0 values of C/Co. (Feed and column effluent TOC concentrations are shown in Figure D-19, Appendix D.)

The above trends are more clearly illustrated in the cumulative curves of Figure 6.2-2. In this figure the abscissa corresponds to the total quantity of organics applied to the column (i.e. $t \cdot \sum_1^n F_I \cdot C_I^0$) where:

F_I : average daily flow rate

C_I^0 : daily average inlet TOC

n : number of days the column is in operation

t : total time of operation in the same time units as F_I

Figure 6.2-1: COMPARISON OF COLUMN BREAKTHROUGH AT THE 4.5 CM BED DEPTH WITH OZONATED AND NON-OZONATED WATER

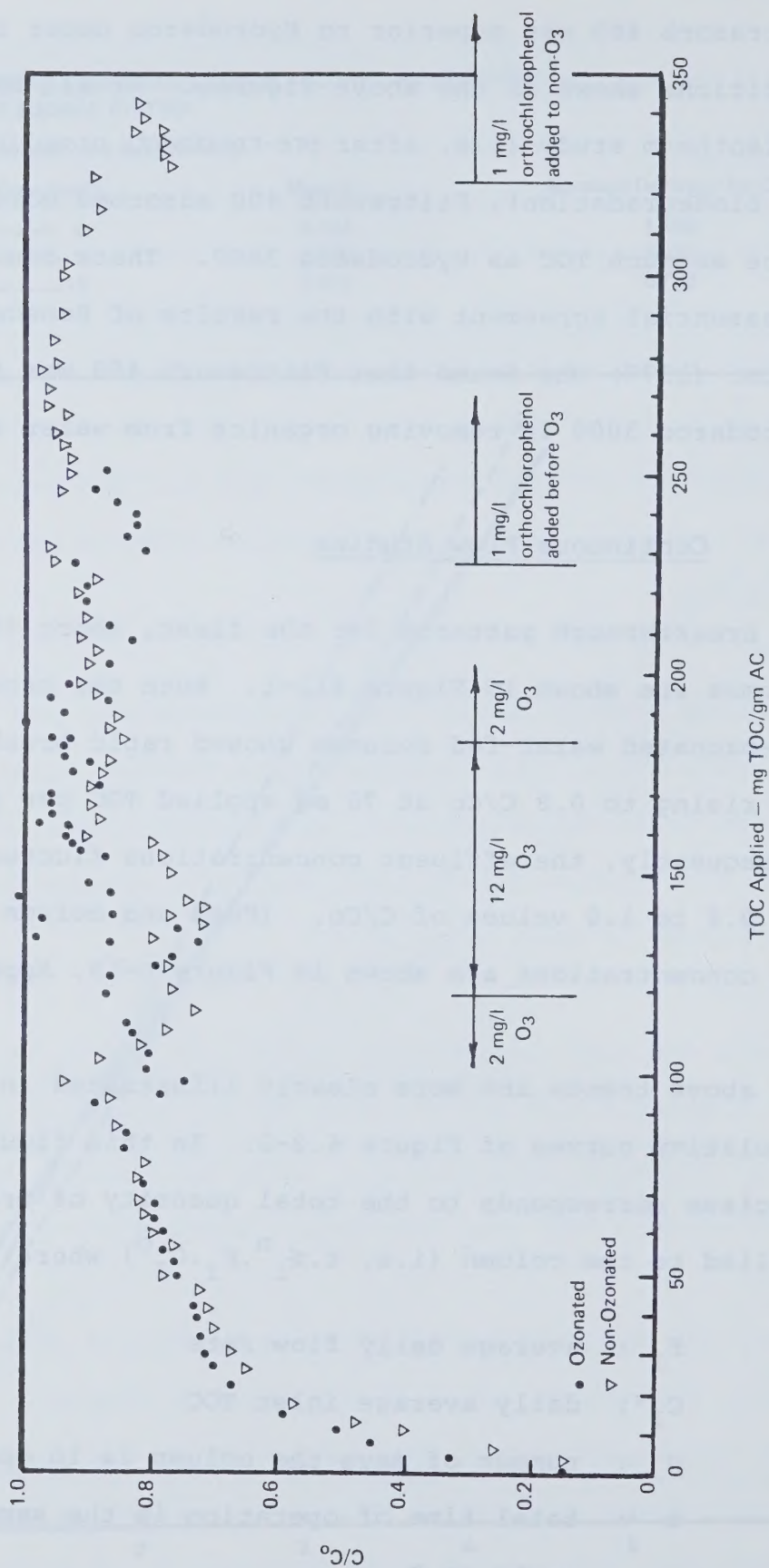
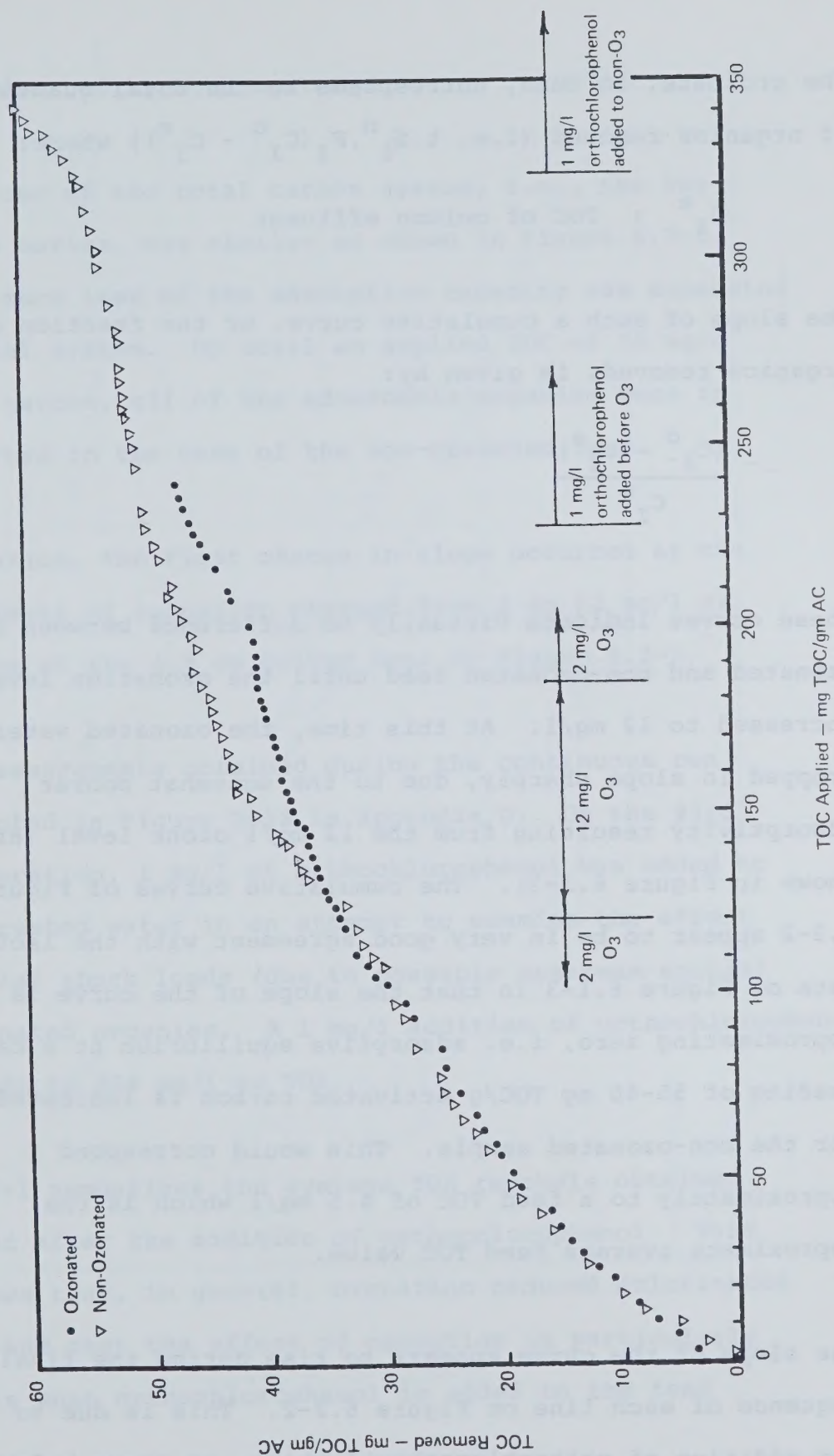


Figure 6.2-2: COMPARISON OF CUMULATIVE TOC REMOVAL FROM OZONATED AND NON-OZONATED SAMPLES IN ACTIVATED CARBON COLUMN (4.5 cm)



The ordinate, in turn, corresponds to the total quantity of organics removed (i.e. $t \cdot \sum_1^n F_I (C_I^O - C_I^e)$) where:

C_I^e : TOC of column effluent

The slope of such a cumulative curve, or the fraction of organics removed, is given by:

$$\frac{(C_I^O - C_I^e)}{C_I^O}$$

These curves indicate virtually no difference between the ozonated and non-ozonated feed until the ozonation level is increased to 12 mg/l. At this time, the ozonated water dropped in slope sharply, due to the somewhat poorer adsorptivity resulting from the 12 mg/l ozone level (as shown in Figure 6.1-3). The cumulative curves of Figure 6.2-2 appear to be in very good agreement with the isotherm data of Figure 6.1-3 in that the slope of the curve is approximating zero, i.e. adsorptive equilibrium at a carbon loading of 55-60 mg TOC/g activated carbon is indicated for the non-ozonated sample. This would correspond approximately to a feed TOC of 4.5 mg/l which is the approximate average feed TOC value.

The slope of the curve appears to rise during the final sequence of each line on Figure 6.2-2. This is due to the addition of orthochlorophenol which, as shown below,

was well adsorbed by both systems.

The behaviour of the total carbon system, i.e., the two columns in series, was similar as shown in Figure 6.2-3, although, much less of the adsorptive capacity was exhausted in the total system. Up until an applied TOC of 35 mg/g activated carbon, all of the adsorbable organics were in fact adsorbed in the case of the non-ozonated feed.

With ozonation, the first change in slope occurred at the time the level of ozonation changed from 2 to 12 mg/l as in the case of the 4.5 cm column data of Figure 6.2-2.

The TOX measurements obtained during the continuous run are presented in Figure D-18 in Appendix D. On the 93rd day of operation, 1 mg/l of orthochlorophenol was added to the pre-treated water in an attempt to examine the effect of potential shock loads (due to possible upstream spills) of chlorinated organics. A 1 mg/l addition of orthochlorophenol corresponds to 224 $\mu\text{g/l}$ as TOX.

Table 6.2-1 summarizes the average TOX removals obtained before and after the addition of orthochlorophenol. This table shows that, in general, ozonation reduced chlorinated organics and that the effect of ozonation is particularly noticeable when orthochlorophenol is added to the feed

Figure 6.2-3: COMPARISON OF CUMULATIVE TOC REMOVAL FROM OZONATED AND NON-OZONATED SAMPLES IN ACTIVATED CARBON COLUMNS (4.5 + 28 cm BED DEPTH)

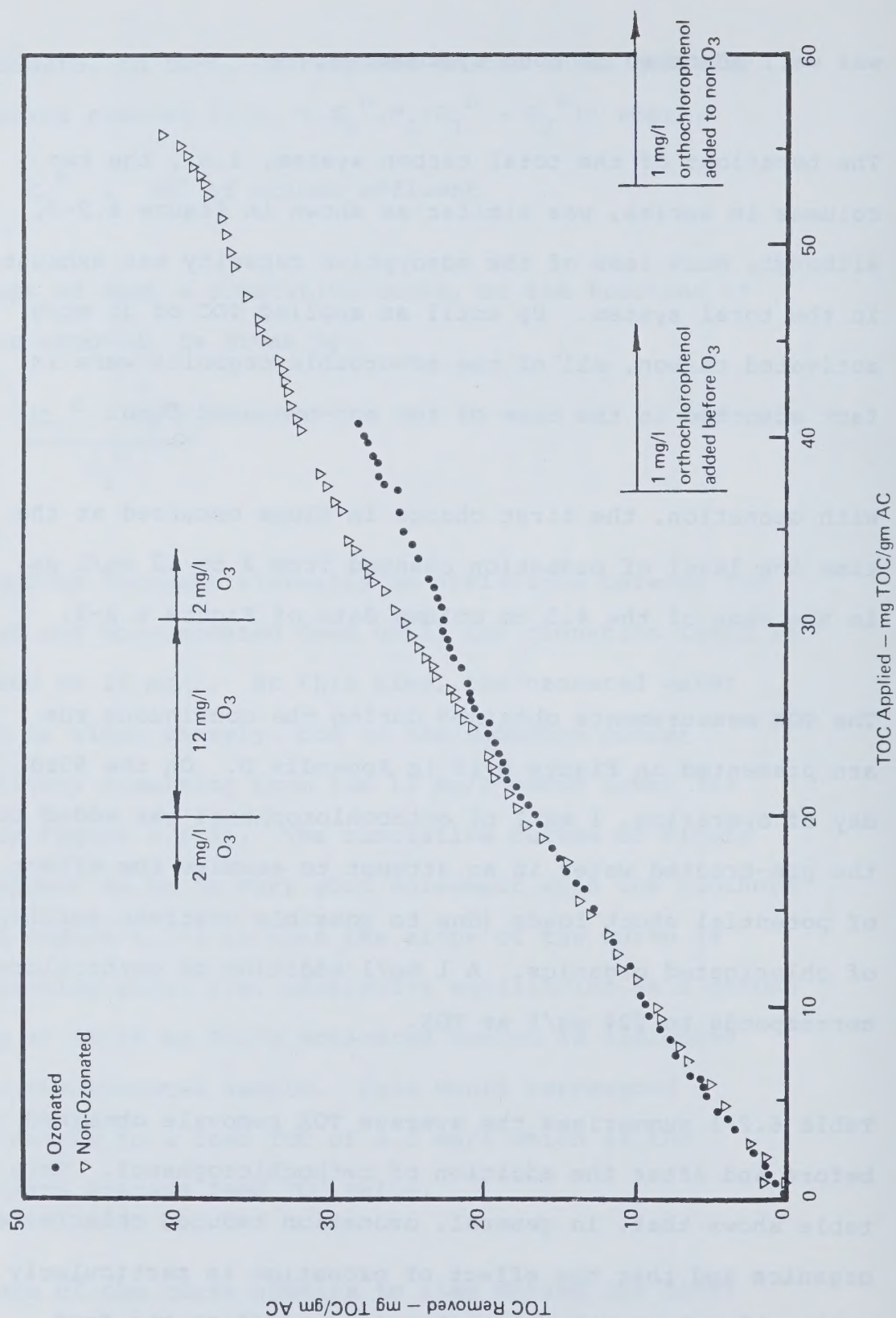


TABLE 6.2-1 AVERAGE TOX CONCENTRATION IN CONTINUOUS-RUN WATER SAMPLES

TOX Concentration ($\mu\text{g/l}$)	Without Orthochlorophenol Addition		With Orthochlorophenol Addition	
	Non-Ozonated	Ozonated	Non-Ozonated	Ozonated
Equivalent TOX added to Pre- treated Water	-	-	224	224
Concentration Applied to 1st (4.5 cm) Carbon Column	6.9	4.8	223	11
Concentration Applied to 2nd (28 cm) Carbon Column	-	-	60	6
Concentration Leaving 2nd (28 cm) Carbon Column	3.6	2.2	6	1

stream. The removal during ozonation could be due to both the reaction with ozone as well as that of conventional oxidation of chloro-organics.

Prior to the addition of orthochlorophenol, activated carbon adsorption tends to remove about 50 percent of the applied chloro-organics. Once the shock load is added, chlorinated organics removal becomes nearly 100% for both ozonated and non-ozonated columns, as shown by Figure 6.2-3 and Table 6.2-1.

The cumulative TOX removal curves across the entire adsorption system is shown in Figure 6.2-4 for the ozonated and non-ozonated waters. Prior to the addition of 1 mg/l of orthochlorophenol only 50% of the applied TOX is removed from the feed. Once a shock loading of 1 mg/l orthochlorophenol is applied, essentially all of the chlorophenol surge is removed by the carbon system which, as noted earlier, was beginning to show signs of adsorptive exhaustion. This indicates the excellent potential of granular activated carbon for preventing the contamination from spills in surface water supplies.

Two sets of column effluents were analyzed for PAH. The results are presented in Table 6.2-2. In the initial period of column operations, (i.e. at applied TOC levels of 2.15 and

Figure 6.2.4: CUMULATIVE TOX REMOVAL AT THE 4.5 + 28 cm BED DEPTH

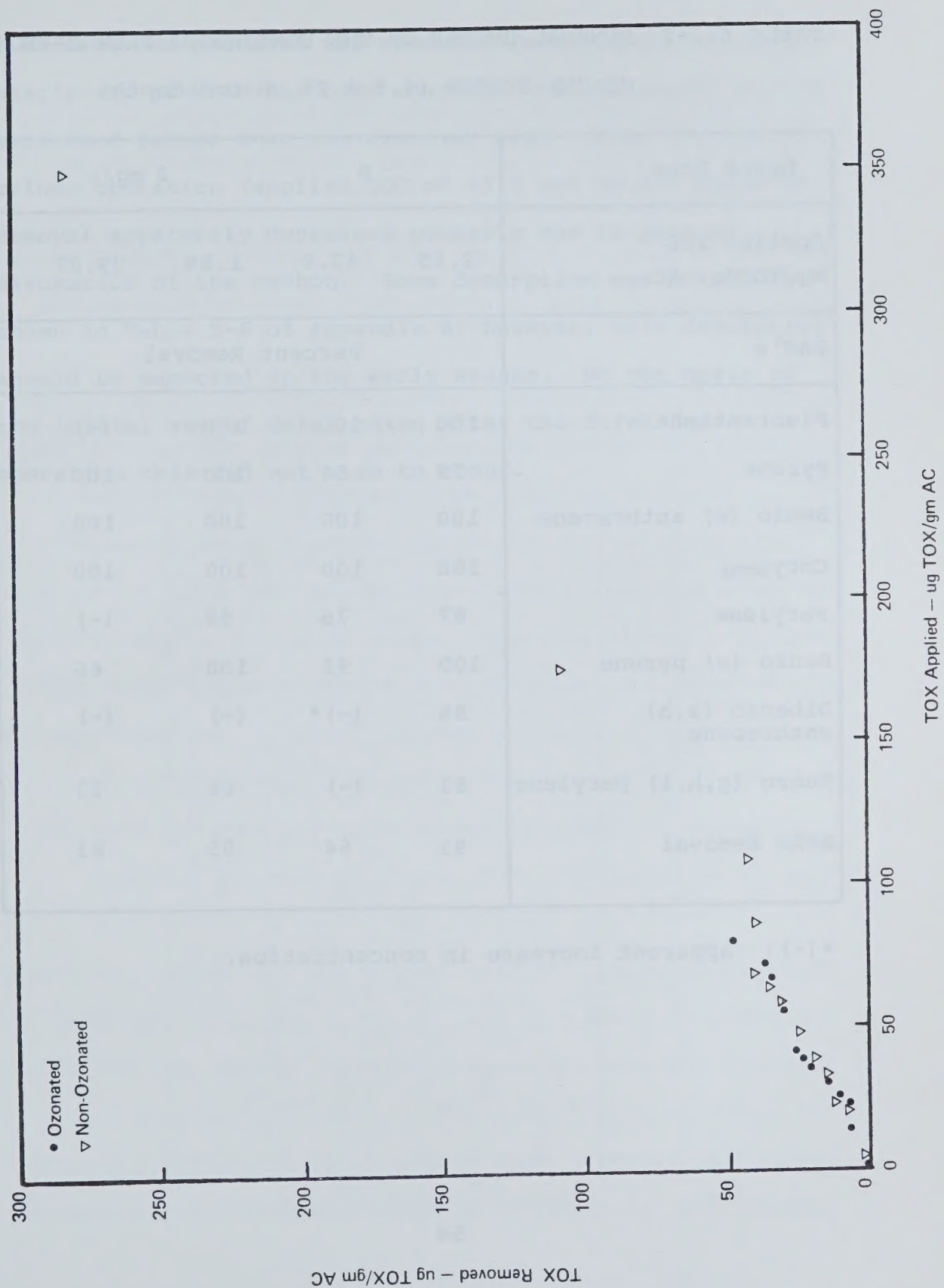


TABLE 6.2-2 REMOVAL OF PAH IN THE CONTINUOUS FLOW CARBON
COLUMN SYSTEM (4.5 + 28 cm bed depth)

Ozone Dose	0		2 mg/l	
Applied TOC mg TOC/g AC	2.15	42.8	1.89	29.87
PAH's	Percent Removal			
Fluoranthene	100	100	100	(-)
Pyrene	79	54	100	100
Benzo (a) anthracene	100	100	100	100
Chrysene	100	100	100	100
Perylene	87	76	98	(-)
Benzo (a) pyrene	100	93	100	66
Dibenzo (a,h) anthracene	96	(-)*	(-)	(-)
Benzo (g,h,i) perylene	83	(-)	88	23
ΣPAH Removal	93	64	95	83

*(-): Apparent increase in concentration.

1.89 from non-ozonated and ozonated feeds respectively), nearly all of Σ PAH has been removed. The ozonated columns performed better than non-ozonated ones. Near the end of column operation (applied TOC of 42.8 and 29.87) the Σ PAH removal apparently decreased probably due to partial saturation of the carbon. Some desorption was noted, as shown in Table B-8 of Appendix B; however, this desorption should be expected in the early stages. On the basis of the initial set of data, taken after the first day's operation this did not seem to occur.

7. OVERALL ORGANIC REMOVALS

The tables in Appendix B, summarize the removal data on a sample-by-sample basis. Table 7-1 is a composite of the batch processing data for the 2 mg/l ozone level. The purpose of Table 7-1 is to show the relative importance of each processing step in the overall removal of organics.

In general, pretreatment removes approximately 35% of the organics (TOC basis) while ozonation removes very little of the organics at the 2 mg/l dosage. Biodegradation removes another 15% and adsorption at a carbon dose of 160 mg/l removes an additional 38% of the TOC. A 160 mg/l dose of powdered activated carbon would be extremely high and, in practice, granular beds would be used. Such beds would initially adsorb a greater fraction but subsequently a smaller fraction of the organics. Depending on the regeneration frequency, the average TOC removal over the life of an adsorption bed, may vary from 10 to 40%.

There is relatively little TOX in the raw water. Furthermore, the observed levels in the raw water are near the detection limit of the TOX measurement method. Hence, the TOX results are prone to significant error. The trends shown in Table 7-1, however, were consistently observed, i.e. ozonation reduced TOX values while biodegradation often resulted in

TABLE 7-1 SUMMARY OF TREATMENT RESULTS (Ozonation step is for 2 mg/l ozone dose, steps after ozonation refer to 2 mg/l O₃ sample and adsorption data is after 160 mg/l of activated carbon addition)

Parameter	Treatment Steps			
	Raw	Pretreatment	Ozonation	Biodegradation Adsorption
TOC - mg/l	7.70	5.06	5.00	1.06
TOX - µg/l	—	2.7	1.6	0.8
ΣPAH - ng/l	1309.7	30.3	3.3	—

TOC, TOX and PAH levels shown here are averages of the seven samples collected.

slight increases. The increase during biodegradation is probably due to contamination from the bacterial seed added to promote biodegradation.

The removal of PAH was generally similar to TOX and occasionally during biodegradation increases in PAH as well as TOC were observed, probably due to contamination of the bacterial seed. Indeed, some of the individual data, as reported in Appendix B (Tables B-1 to B-8) exhibited anomalous behaviour. On the whole, however, and as noted in Table 7-1, the most substantial removals of PAH were observed during ozonation. The levels and amounts of PAH were insufficient for estimating the removals of PAH during batch adsorption studies. On the other hand, continuous adsorption studies, as noted in Section 6.2, showed excellent PAH removals.

8. CONCLUSIONS

The following conclusions are derived from this study:

- (i) A substantial portion of the raw water organics (approximately 35% of the TOC) can be reduced by coagulation, sedimentation and filtration pretreatment. PAH levels are also drastically reduced by such pretreatment.
- (ii) Almost all of the remaining organics can be removed by the combination of ozonation, biodegradation and activated carbon adsorption.
- (iii) Ozonation alone appears to be very efficient in removing PAH, even at applied ozone levels as low as 2 mg/l. Ozonation, on the other hand, is shown to be somewhat less efficient in removing or reducing TOC.
- (iv) TOC removal is best accomplished by biodegradation plus activated carbon adsorption.
- (v) Ozonation generally improves the biodegradation of the organics without significant alteration in adsorptivity.

- (vi) In the continuous adsorption column experiments, slightly better organics removals are obtained from those samples not undergoing pre-ozonation.
- (vii) Shock loads (1 mg/l) of orthochlorophenol are completely damped out by the continuous flow adsorption columns.

REFERENCES

- Shackelford, W.N., and Keith, L.H., 1976
Frequency of Organic Compounds Identified
in Water. U.S.E.P.A. Report 600/4-76-062
- Benoit, F.N., LeBel, G.L., and Williams, D.T., 1979
International J. of Environmental Analytical
Chemistry. 6, 277
- Benedek, A. and Bancsi, J.J., 1977
A Study of the Removal of Synthetic Organics
from Drinking Water by Activated Carbon.
Health and Welfare Canada, 77-EHD-17, Dec. 1977
- Kuhn, W., Sontheimer, H., Steiglitz, L., Maier, B.
and Kurz, R., 1978
Use of Ozone and Chlorine in Water Utilities in
the Federal Republic of Germany.
J. AWWA, 70, 326, June 1978
- Benedek, A., 1977
The Effect of Ozone on Activated Carbon Adsorption -
A Mechanistic Analysis of Water Treatment Data.
I.O.I. Symposium on Advanced Ozone Technology,
Toronto, Canada. Nov. 16-18, 1977
- Benedek, A., 1974
Carbon Evaluation and Process Design; Physical -
Chemical Treatment. Activated Carbon Adsorption
in Water Pollution Control.
Technology Transfer Seminar. Ottawa, Canada.
Oct. 24, 1974
- Schalekamp, M., 1975
Translation of Reports on Special Problems of Water
Technology. Vol. 9, Adsorption.
Proceedings of a Conference held at the Engler
Bunte Institute fur Wasser-Chemie.
Karlsruhe, Fed. Rep. of Germany.
EPA 600/9-76-030
- Nicholson, A.A. and Meresz, O., 1976
Organics in Ontario Drinking Waters; Part I.
The Occurrence and Determination of Free
and Total Potential Haloforms.
Proc. Pittsburgh Conference of Analytical
Chemistry and Applied Spectroscopy.
March 3, 1976

APPENDIX A

DETAILED ANALYTICAL METHODS

A.1 Total Organic Carbon (TOC)

Total Organic Carbon (TOC) is determined by the difference between the total carbon (TC) and the inorganic carbon (IC) in the sample.

The TOC is determined by the difference between the total carbon (TC) and the inorganic carbon (IC) in the sample.

The TOC is determined by the difference between the total carbon (TC) and the inorganic carbon (IC) in the sample.

The TOC is determined by the difference between the total carbon (TC) and the inorganic carbon (IC) in the sample.

The TOC is determined by the difference between the total carbon (TC) and the inorganic carbon (IC) in the sample.

The TOC is determined by the difference between the total carbon (TC) and the inorganic carbon (IC) in the sample.

The TOC is determined by the difference between the total carbon (TC) and the inorganic carbon (IC) in the sample.

A.2 Ultra-violet Spectrophotometry

UV absorbance, at the wavelength of 254 nm, is measured with a bench top bench Spectrophotometer 11-000 spectrophotometer with this instrument sample cells up to 10 cm are used.

For studies with portable water systems, the method light path length, 10 cm with this instrument, was used for analysis.

APPENDIX A

DETAILED ANALYTICAL METHODS

A.1 Total Organic Carbon (TOC)

Total Organic Carbon is determined using the Dohrman DC-54 Ultra Low Level TOC Analyzer.

The analysis scheme involves UV oxidation (in the presence of persulfate) of organics. The resulting CO_2 is stripped from the samples by a helium stream and reduced to methane. The methane is detected by an FID (Flame Ionization Detector). The TOC detection limit is about 10 $\mu\text{g/l}$ and reproducibility is about $\pm 25 \mu\text{g/l}$.

Good recoveries were indicated for several organic compounds by Takahashi (1976).

A.2 Ultra-violet Absorbance ($A_{254}^{10 \text{ cm}}$)

UV absorbance, at the wavelength of 253.7 nm is measured with a Bausch and Lomb Spectronic 21-UVD spectrophotometer. With this instrument sample cells up to 10 cm can be used.

For studies with potable water systems, the maximum light path length, 10 cm with this instrument, was used for maximum sensitivity.

The absorbance of the empty cell is set at 0.100 for all measurements to obtain a reliable "zero" base line as it is impossible to obtain organics-free water.

A.3 Total Organic Halogen (TOX)

Initially, the total organic halogen analysis was based on the method of Kuhn and Sontheimer (1973). This involves adsorbing the organic halogen on activated carbon and selectively desorbing the inorganic halides in a parallel experiment. By subtracting the inorganic value from the total obtained from the pyrohydrolysis of the carbon sample and halide determination on the condensate, TOX values are obtained. This method, however, was found to be unsatisfactory due to the inefficient desorption of the inorganic chlorides, thus yielding high values.

This laboratory attempted to eliminate the inorganic chloride by precipitating with silver, (Fackelmann, 1978). Experiments showed that this method is also unsatisfactory as reliable background values could not be obtained due to the differing chloride levels present, and as different samples required varying amounts of silver. Furthermore, as precipitation by silver is not 100%, varying amounts of inorganic chloride remained in the sample to adsorb onto the carbon. Thus each sample required its own unique blank.

A short study indicated that solvent extraction by ether does not extract inorganic chloride from the water layer. Therefore it was decided to opt for total organic halogen measurements along the lines of Glaze et al (1977).

The process involves the adsorption of halogenated organics from a 500 ml water sample passed through a column containing a 5 cm high x 1 cm in diameter bed of XAD-2 resin (Rohm and Haas Co.) at a flowrate of 10-15 ml/min. The non-polar halogenated organics are extracted from the resin by ethyl ether (distilled in glass, Caledon Laboratories, Ltd.). A portion of the ether is allowed to replace the water and remain in the column for 10 minutes, and the balance passed through the column at 10 ml/min. 0.5 ml benzyl ether (Eastman Chem., b.p. = 298°C) is added to the extract and evaporated to 0.5 ml. A 20 µl portion is introduced into the Dohrman MCTS-20 Microcoulometer for halide determination in terms of Cl^- .

The instrument detection limit is 0.1 µg/l. Reproducibility is $\pm .2$ µg/l.

The XAD-2 resin is regenerated in situ by rinsing with 50 ml methanol, 30 ml ethyl ether; 30 ml acetone and 50 ml of distilled water passed through, sequentially, ion exchange resin (Barnstead Co.'s ultrapure (mixed bed) #D8902), activated

carbon and ion exchange resin columns. TOX was not detected in this water and its TOC is less than 0.2 mg/l. The solvents (all distilled in glass, Caledon Laboratories, Ltd.) are allowed to remain in the column for 5 minutes and the balance passed through the column at 10 ml/min.

A.4 Polycyclic Aromatic Hydrocarbons (PAH)

The determination of the Polynuclear Aromatic Hydrocarbons is based on the method of Smillie et al (1978) with the extraction procedure adapted to water samples.

The extraction procedure involves the adsorption of the PAH from water samples on to XAD-2 resin bed 24 cm high x 4 cm in diameter, in a column. The resin is conditioned by successively washing with 1 litre of water distilled in glass from KMnO_4 solution. All solvents used are spectrograde quality (Caledon Laboratories, Ltd.). Whenever possible, a 10 litre sample is passed through the column at a flowrate of less than 2 bed volumes/min.

The PAH are eluted by 250 ml ethyl ether. The ether remains in the column for about 25 minutes and then is drained and collected. The extract is dried over 20 g of anhydrous Na_2SO_4 . The Na_2SO_4 is washed with three portions of 10 ml ether. The washings and the extract are placed in a pear-

shaped flask and reduced to 2 ml in a Buchler Flash evaporator. The extract is further reduced to 1 ml under a stream of dry N₂ gas. The extracts are stored in the dark at about 3-4°C in a refrigerator.

The XAD-2 resin is prepared for use by washing the resin in batches with methanol until the fines are removed. Then the resin is successively Soxhlet extracted with 300 ml of methanol, 300 ml of acetonitrile, and 300 ml of ethyl ether, each for 8 hours. The clean resin is stored under methanol.

The detection system for the PAH is the Varian Model 8500 Liquid Chromatograph, the Varian 635 UV-Visible Spectrophotometer and the Turner Model 111 Fluorometer according to the method of Smillie et al (1978).

The detection limit for the liquid chromatograph system is 0.2-0.5 µg/ml extract depending upon the individual PAH; and reproducibility of $\pm 10\%$. Recoveries of PAH from the XAD-2 resin columns are about 81-93%. (Psarakis, 1978).

Suspended matter is filtered out of the water sample with fiber glass filters (Sartorius), and Soxhlet extracted overnight with 300 ml of ethyl ether. The extract is concentrated to 1 ml as stated before. An equal number of empty filters is also extracted to determine interference from the filters.

A.5 Chemical Oxygen Demand

The determination of Chemical Oxygen Demand is based on the method of Maier (1973).

This method is similar to EPA method (Soret No. 00335). The modifications include the use of weaker dichromate solution depending upon expected COD in the sample (for COD = 0.2 - 5 mg/l, 0.004 N dichromate; for 5 - 20 mg/l, 0.008 N; and for 20 - 100 mg/l 0.016 N), a sample size of 50 ml, and the sample is incubated with the reagents at 140°C for 4 hours in sealed containers. The balance of the procedure follows Standard Methods.

The detection limit is estimated to be 0.3 mg/l with a precision of approximately $\pm 3\%$ (Maier 1973).

A.6 Ozone Residual

The determination of ozone residual in water follows Standard Methods (1975) iodometric method (No. 423A), where the free iodine liberated by ozone from a potassium iodide solution is titrated with standard sodium thiosulfate under acidic conditions.

REFERENCE

1. Anon (1975).
Standard Methods for the Examination of Water and Wastewater.
14th Edition, APHA - AWWA - WPCF.
2. Fackelmann, A. (1978).
Measurement of Total Halogenated Organic Level in Ontario Water and Wastewater Treatment Plant Samples. Unpublished report, Water Research Group, Dept. of Chem. Eng., McMaster University, Hamilton, Ont.
3. Glaze, W.H., Peyton, G.R. and Rowley, R. (1977).
Total Organic Halogen as Water Quality Parameter: Adsorption/Microcoulometric Method.
Environ. Sci. and Tech. 11, 7, 685.
4. Kuhn, W. and Sontheimer, H. (1973).
Einige Untersuchungen zur Bestimmung von Organischen Chlorverbindungen auf aktivkohlen.
Vom Wasser, 41, 65.
5. Maier, D. (1973).
Eine Verbesserte Methode zur Bestimmung des Chemischen Sauerstoffbedarfs mit Kaliumdichromat (COD-Methode).
gwf-wasser/abwasser, 114, H. 8, 366.
6. Psarakis, S. (1978).
The Analysis of Polycyclic Aromatic Hydrocarbons in Water. Unpublished report, Water Research Group, Dept. of Chem. Eng., McMaster University, Hamilton, Ontario.
7. Smillie, R.D., Wang, D.T. and Meresz, O. (1978).
The Use of Combination of Ultraviolet and Fluorescence detectors for the Selective detection and Quantitation of Polynuclear Aromatic Hydrocarbons by High Pressure Liquid Chromatograph.
J. Environ. Sci. Health, A13, (1), 47.
8. Takahashi, Y. (1976).
Ultra Low Level TOC Analysis of Potable Waters.
Presented at: Water Quality Technology Conference, AWWA, Dec. 5-8, 1976.

TABLE B-1 Sample No. 1

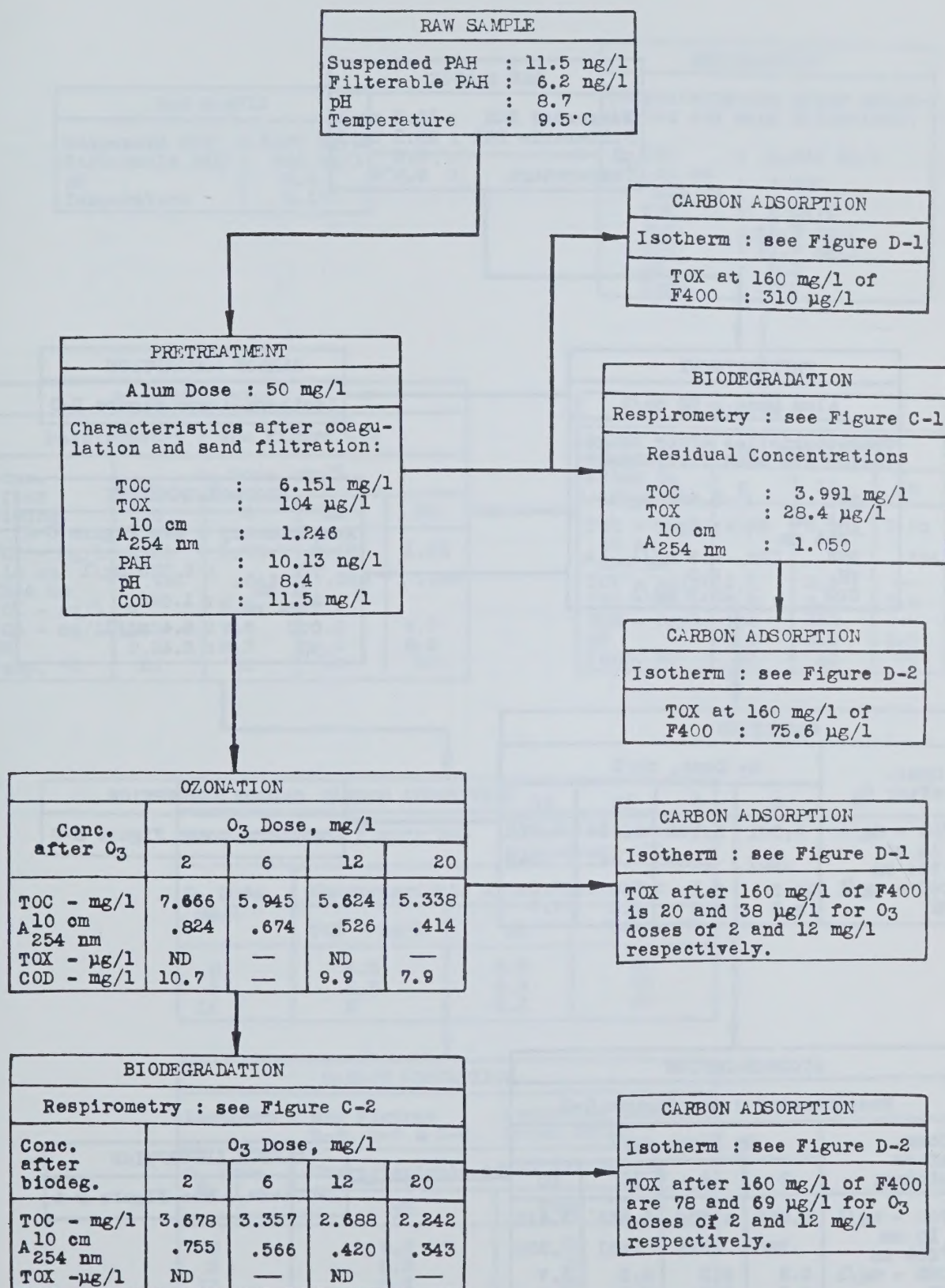


TABLE B-2 Sample No. 2

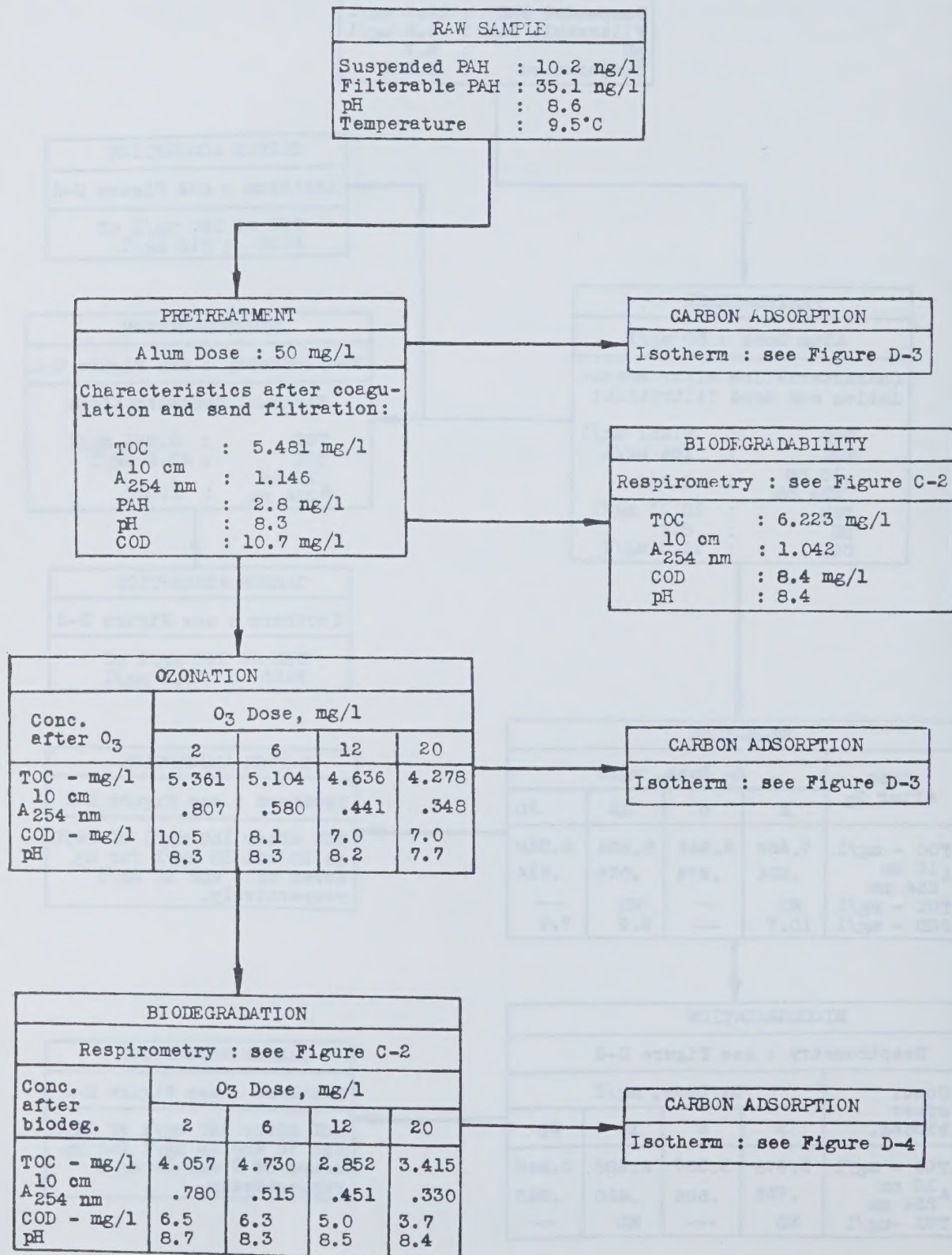


TABLE B-3 Sample No. 3

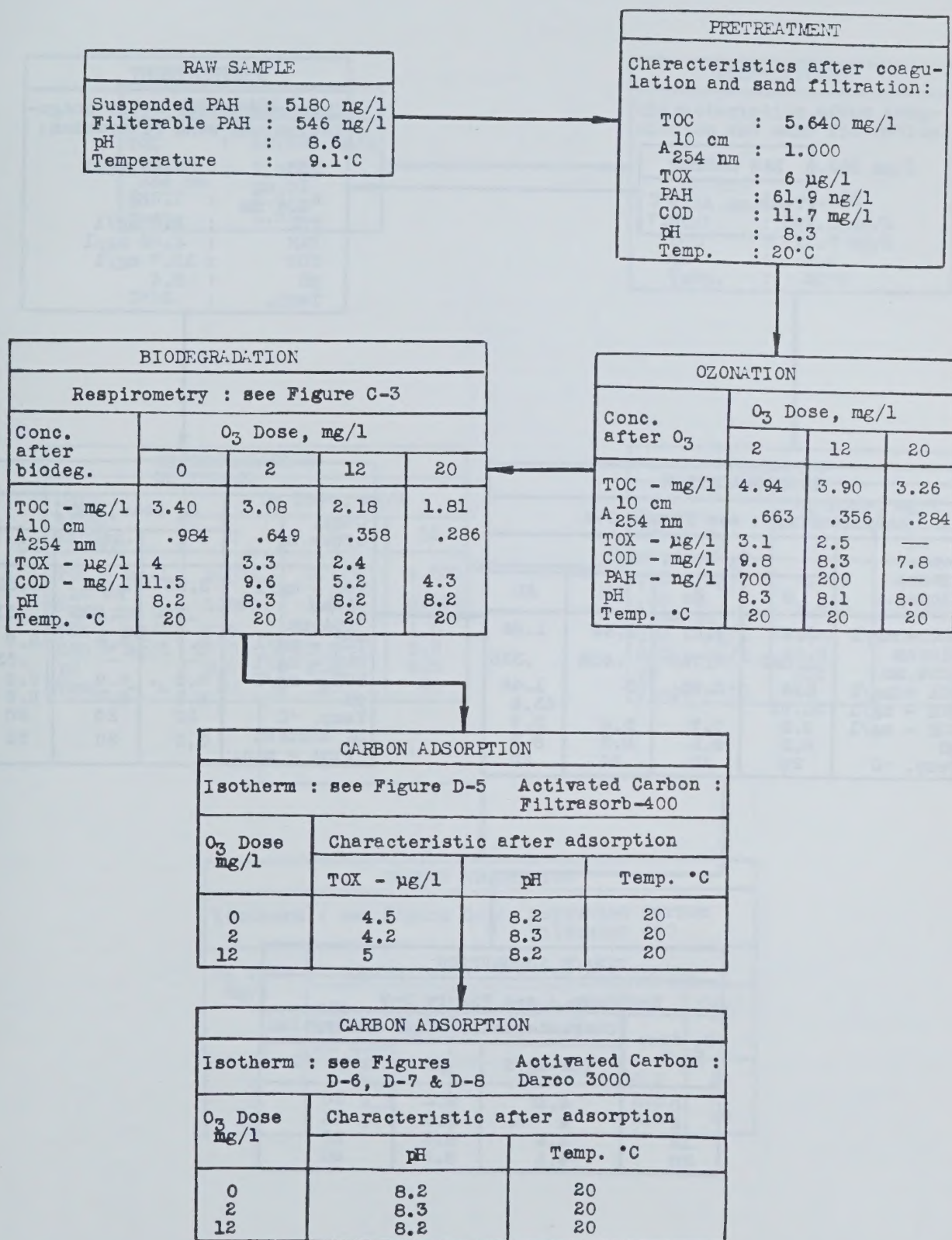


TABLE B-4 Sample No. 4

RAW SAMPLE	
Temp.	: 9°C
pH	: 8.7

PRETREATMENT	
Characteristics after coagulation and sand filtration:	
TOC	: 3.65 mg/l
10 cm	
A ₂₅₄ nm	: 1.083
TOX	: 2.0 µg/l
PAH	: 4.06 ng/l
COD	: 10.7 mg/l
pH	: 8.4
Temp.	: 20°C

BIODEGRADATION				
Respirometry : see Figure C-4				
Conc. after biodeg.	O ₃ Dose, mg/l			
	0	2	12	20
TOC - mg/l	3.97	3.47	2.44	1.86
A _{10cm}				
A ₂₅₄ nm	1.062	.760	.408	.336
TOX - µg/l	3.4	3.83	3	1.44
PAH - ng/l	50.95			63.4
COD - mg/l	9.5	7.7	5.2	3.7
pH	8.2	8.3	8.3	8.2
Temp. °C	20	20	20	20

OZONATION			
Conc. after O ₃	O ₃ Dose, mg/l		
	2	12	20
TOC - mg/l	3.53	2.91	2.52
A _{10cm}			
A ₂₅₄ nm	.772	.406	.310
TOX - µg/l	2.7	3.8	2.7
PAH - ng/l	—	—	.33
COD - mg/l	8.8	6.9	6.4
pH	8.3	8.2	8.2
Temp. °C	20	20	20
O ₃ contact time - min.	3.5	20	35

CARBON ADSORPTION			
Isotherm : see Figure D-9			
O ₃ dose mg/l	Characteristic after adsorption		
	TOX-mg/l	pH	Temp. °C
0	4.1	8.2	20
2	4	8.3	20
12	2.9	8.3	20
20	4.1	8.2	20

TABLE B-5 Sample No. 5

RAW SAMPLE				PRETREATMENT			
TOC : 10.266 mg/l A _{10 cm} : 1.930 pH : 8.6 Temp. : 0.5°C				Characteristics after coagulation and sand filtration: TOC : 6.693 mg/l A _{10 cm} : 1.860 TOX : 2.0 µg/l COD : 12.7 mg/l pH : 8.4 Temp. : 20°C			
BIODEGRADATION				OZONATION			
Conc. after biodeg.	O ₃ Dose, mg/l			Conc. after O ₃	O ₃ Dose, mg/l		
	0	2	12		2	12	
TOC - mg/l	6.534	6.179	4.305	TOC - mg/l	6.216	4.872	
A _{10 cm}	1.840	1.570	0.866	A _{10 cm}	1.620	0.922	
A _{254 nm}				A _{254 nm}			
TOX - µg/l	2.9	3.0	1.0	TOX - µg/l	0.8	0.5	
COD - mg/l	12.0	10.5	5.8	COD - mg/l	10.9	4.0	
pH	8.5	8.6	8.5	pH	8.5	8.3	
Temp. - °C	20	20	20	Temp. - °C	20	20	
CARBON ADSORPTION							
Isotherm : see Figure D-10 Activated Carbon Filtrisorb 400							
O ₃ Dose mg/l	Characteristic after adsorption						
	TOX - µg/l at 160 mg/l AC dose	Nonadsorbable TOC - mg/l	pH	Temp. °C			
0	15.9	0.3	8.5	20			
2	4.3	0	8.6	20			
12	5.7	0.4	8.5	20			

TABLE B-6 Sample No. 6

RAW SAMPLE	
TOC	: 8.005 mg/l
A _{10 cm}	: 1.810
pH	: 8.6
Temp.	: 0.5°C

PRETREATMENT	
Characteristics after coagulation and sand filtration:	
TOC	: 4.638 mg/l
A _{10 cm}	: 1.224
TOX	: 3.5 µg/l
PAH	: 72.5 ng/l
COD	: 10.2 mg/l
pH	: 8.3
Temp.	: 20°C

BIODEGRADATION			
Respirometry : See Figure C-6			
Conc. after biodeg.	O ₃ Dose, mg/l		
	0	2	12
TOC - mg/l	4.595	4.279	2.552
A _{10 cm}	1.234	1.033	0.446
A _{254 nm}			
TOX - µg/l	1.6	2.1	1.1
PAH - ng/l	5.7	0.8	—
COD - mg/l	7.6	6.9	2.5
pH	8.6	8.5	8.4
Temp. °C	20	20	20

OZONATION		
Conc. after O ₃	O ₃ Dose, mg/l	
	2	12
TOC - mg/l	4.409	3.007
A _{10cm}	1.030	0.460
A _{254 nm}		
TOX - µg/l	2.9	0.9
PAH - ng/l	5.9	—
COD - mg/l	7.6	4.0
pH	8.3	8.1
Temp. °C	20	20

CARBON ADSORPTION				
Isotherm : see Figure D-11 Activated Carbon Filtrasorb 400				
O ₃ Dose mg/l	Concentration after adsorption			
	TOX - µg/l at 160 mg/l AC dose	Nonadsorbable TOC - mg/l	pH	Temp. °C
0	9.3	0.1	8.6	20
2	12	0.3	8.5	20
12	9.6	0.3	8.4	20

TABLE B-7 Sample No. 7

RAW SAMPLE	
TOC	: 4.837 mg/l
10 cm	
A ₂₅₄ nm	: 1.510
TOX, filtered	: 0.3 µg/l
TOX, suspended	: 1.2 µg/l
PAH, filtered	: 0.9 ng/l
PAH, suspended	: 37.2 ng/l
COD	: 12.5 mg/l
pH	: 8.4
Temperature	: 0.5°C

PRETREATMENT	
Characteristics after coagulation and sand filtration:	
TOC	: 3.154 mg/l
10 cm	
A ₂₅₄ nm	: 0.894
TOX	: ND
COD	: 7.3 mg/l
pH	: 8.3
Temp.	: 20°C

OZONATION				
Conc. after O ₃	O ₃ Dose, mg/l			
	2	6	12	20
TOC - mg/l	2.819	2.484	2.389	2.205
10 cm				
A ₂₅₄ nm	0.752	0.443	0.328	0.217
TOX - µg/l	ND	ND	ND	ND
COD - mg/l	5.5	4.1	2.9	2.2
pH	8.25	8.15	8.0	7.9
Temp. °C	20	20	20	20

BIODEGRADATION					
Respirometry ; see Figure C-7					
Conc. after biodeg.	O ₃ Dose, mg/l				
	0	2	6	12	20
TOC - mg/l	3.087	2.783	2.360	1.912	1.453
10 cm					
A ₂₅₄ nm	0.855	0.718	0.430	0.275	0.270
TOX - µg/l	ND	ND	0.4	0.1	0.5
COD - mg/l	4.6	5.2	3.4	2.3	2.0
pH	8.3	8.4	8.4	8.4	8.4
Temp. °C	23	23	23	23	23

CARBON ADSORPTION				
Isotherm : see Figure D-13 Activated Carbon Filtrasorb 400				
O ₃ Dose mg/l	Concentration after adsorption			
	TOX - µg/l at 160 mg/l AC dose	Nonadsorbable TOC - mg/l	pH	Temp. °C
0	5.2	0.2	8.3	20
2	2.6	0.2	8.4	20
6	0.4	0.25	8.4	20
12	2.3	0.2	8.4	20
20	7.4	0.2	8.4	20

CARBON ADSORPTION				
Isotherm : See Figure D-12 Activated Carbon Filtrasorb 400				
O ₃ Dose mg/l	Concentration after adsorption			
	TOX - µg/l at 160 mg/l AC dose	Nonadsorbable TOC - mg/l	pH	Temp. °C
0	11.4	0.1	8.3	20
2	0.8	0	8.2	20
6	4.1	0	8.1	20
12	3.8	0	8.0	20
20	5.9	0.15	7.9	20

TABLE B-8 : Detailed List of PAH Analysis Results

All units : ng/l unless otherwise noted ND : Not Detected	FLUORANTHENE	PYRENE	BENZO (a) ANTHRACENE	CHRYSENE	PERYLENE	BENZO (k) FLUORANTHENE	BENZO (a) PERYLENE	DIBENZO (a,h) ANTHRACENE	BENZO (g,h,i) PERYLENE	TOTAL
SAMPLE										
<u>01 - 27/9/78</u>										
Raw - Filterable	ND	1.7	1.0	3.0	0.52	ND	0.01	—	—	6.23
Raw - Suspended	ND	ND	5.28	3.0	2.5	0.7	0.05	—	—	11.53
Coagulated & sand filtered	ND	2.7	2.9	4.0	0.32	0.09	0.12	—	—	10.13
<u>02 - 18/10/78</u>										
Raw - Filterable	12.0	3.7	5.15	11.7	1.89	0.07	0.56	—	—	35.07
Raw - Suspended	4.6	3.7	0.5	1.3	0.05	0.03	0.01	—	—	10.19
Coagulated & sand filtered	1.7	0.2	0.05	0.4	0.29	0.1	0.06	—	—	2.80
<u>03 - 1/11/78</u>										
Raw - Filterable	100	24	110	160	43	28	1.5	516	74	546.1
Raw - Suspended	1250	333	1177.4	1899	227	127	113	2	50	5178
Coagulated & sand filtered	24.4	15.3	8.6	6.5	1.8	0.4	0.5	1.5	2.7	61.7
Coagulated, sand filtered and ozonated (2 mg/l)	ND	ND	ND	ND	0.3	—	ND	0.1	0.3	0.7
Coagulated, sand filtered and ozonated (12 mg/l)	ND	ND	ND	ND	0.1	—	0.2	0.3	0.04	0.2
<u>06 - 17/1/79</u>										
Coagulated and sand filtered	18.3	8.1	17.3	24.6	1.5	—	0.4	1.0	1.2	72.4
Coagulated, sand filtered and ozonated (2 mg/l)	ND	0.5	ND	ND	3.6	—	ND	ND	1.7	5.8
Coagulated, sand filtered, ozo- nated & biodegraded	ND	0.1	1.6	ND	0.5	—	0.5	1.4	1.6	5.7
Coagulated, sand filtered, ozo- nated (2 mg/l) and biodegrad- ed	ND	ND	ND	ND	0.3	—	0.1	0.3	0.1	0.8
Biodegradation Blank	ND	ND	ND	ND	0.1	—	0.02	0.05	0.1	0.3
<u>07 - 5/3/79</u>										
Raw - Filterable	ND	0.4	ND	ND	0.2	—	0.03	0.04	0.2	0.9
Raw - Suspended	9.4	5.7	3.7	5.1	3.1	—	2.4	1.2	6.7	37.3
Column Effluent (9/2/79-10/2/79) non-ozonated	ND	1.7	ND	ND	0.2	—	ND	0.04	0.2	2.1
Column Effluent (9/2/79-10/2/79) ozonated (2 mg/l)	ND	ND	ND	ND	0.06	—	ND	0.05	0.2	0.3
Column Effluent (20/4/79) non-ozonated	3.7	6.3	1.2	ND	2.5	—	1.1	0.3	2.1	17.2
Column Effluent (20/4/79) ozonated (2 mg/l)	ND	13.7	1.0	ND	0.03	—	0.2	0.3	1.3	16.6
Column Effluent (20/4/79) non-ozonated	ND	2.9	ND	ND	0.6	—	0.08	0.45	2.1	6.2
Column Effluent (20/4/79) ozonated (2 mg/l)	0.6	ND	ND	ND	0.6	—	0.1	0.4	1.0	2.7
Activated Carbon (F-400) desorption (ng/g AC)	2.0	2.5	6.1	5.8	1.5	0.6	0.6	1.7	2.1	22.9

APPENDIX C

BIODEGRADATION DATA

Figure C-1: RESPIROMETRIC OXYGEN UPTAKE FOR OZONATED GRAND RIVER WATER
Sample 1

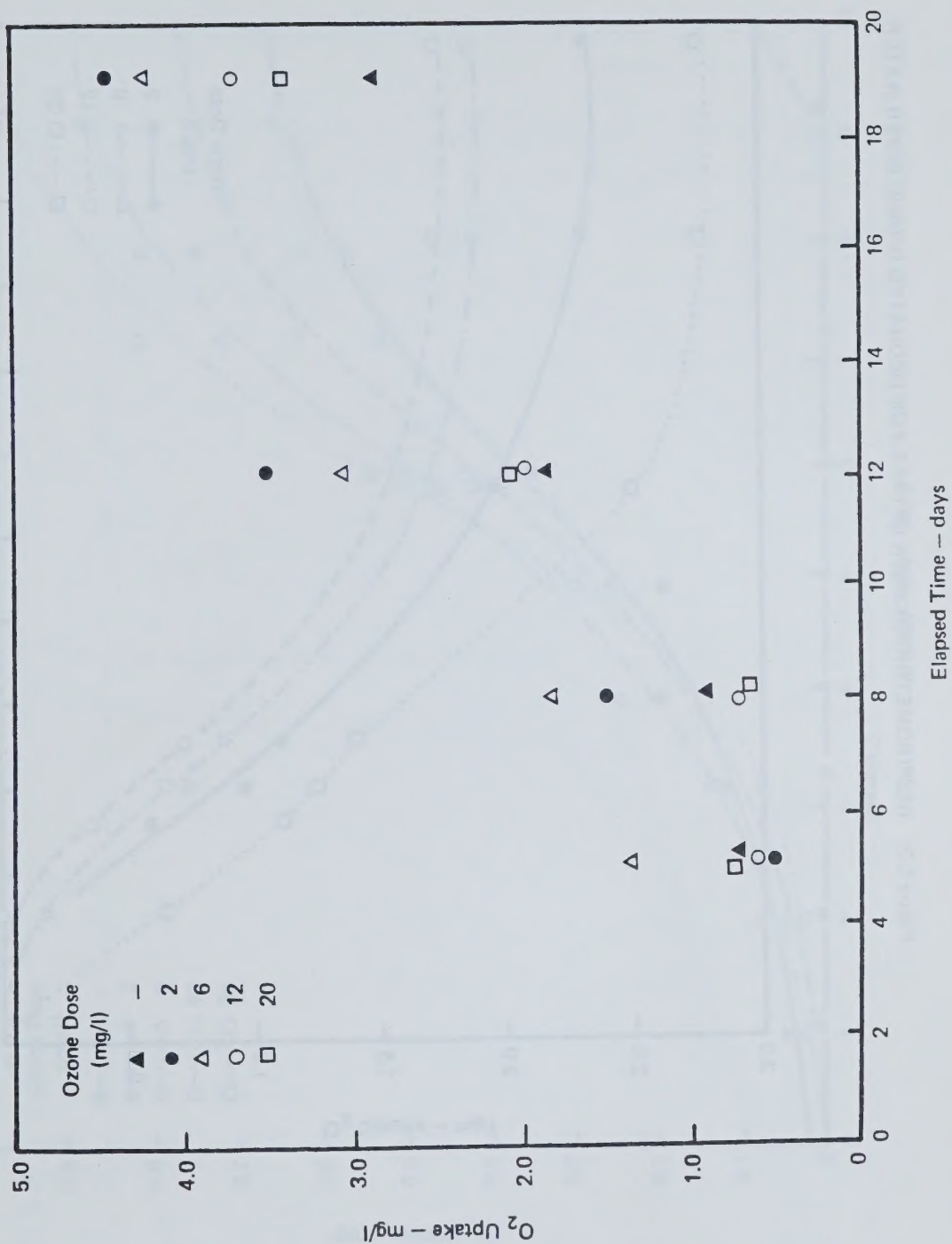


Figure C-2: RESPIROMETRIC OXYGEN UPTAKE FOR OZONATED GRAND RIVER WATER
Sample 2

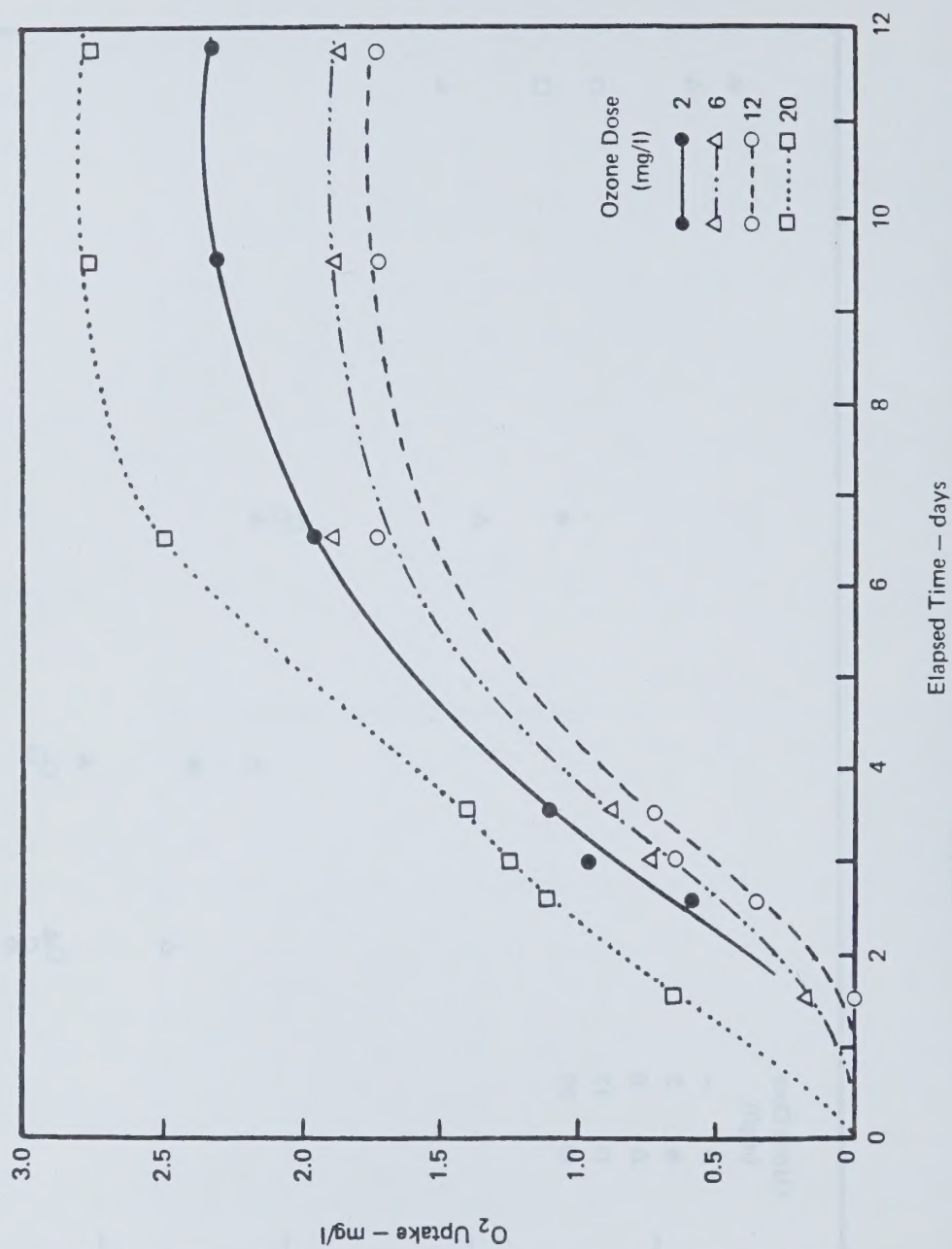


Figure C-3: RESPIROMETRIC OXYGEN UPTAKE FOR OZONATED GRAND RIVER WATER
Sample 3

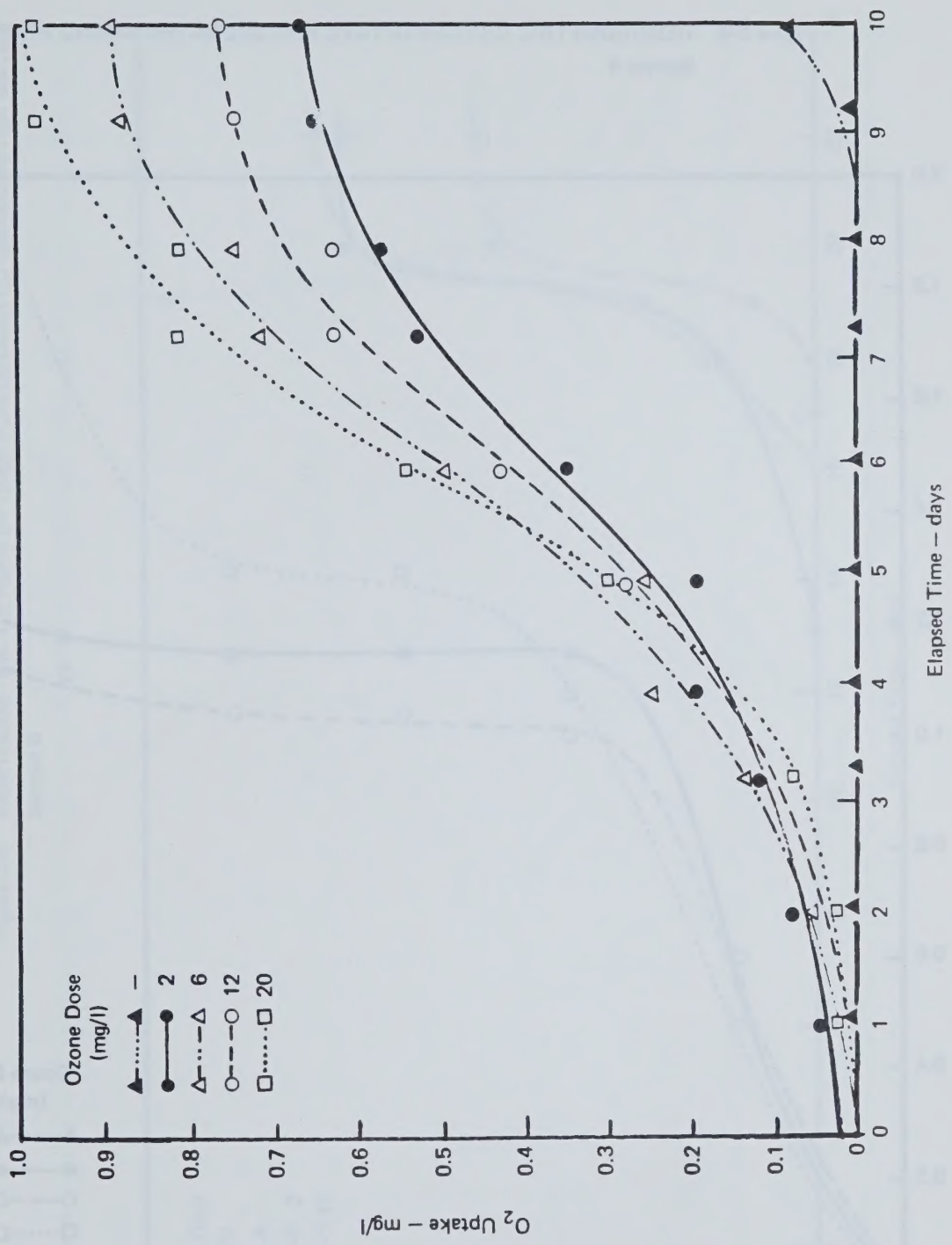


Figure C-4: RESPIROMETRIC OXYGEN UPTAKE FOR OZONATED GRAND RIVER WATER
Sample 4

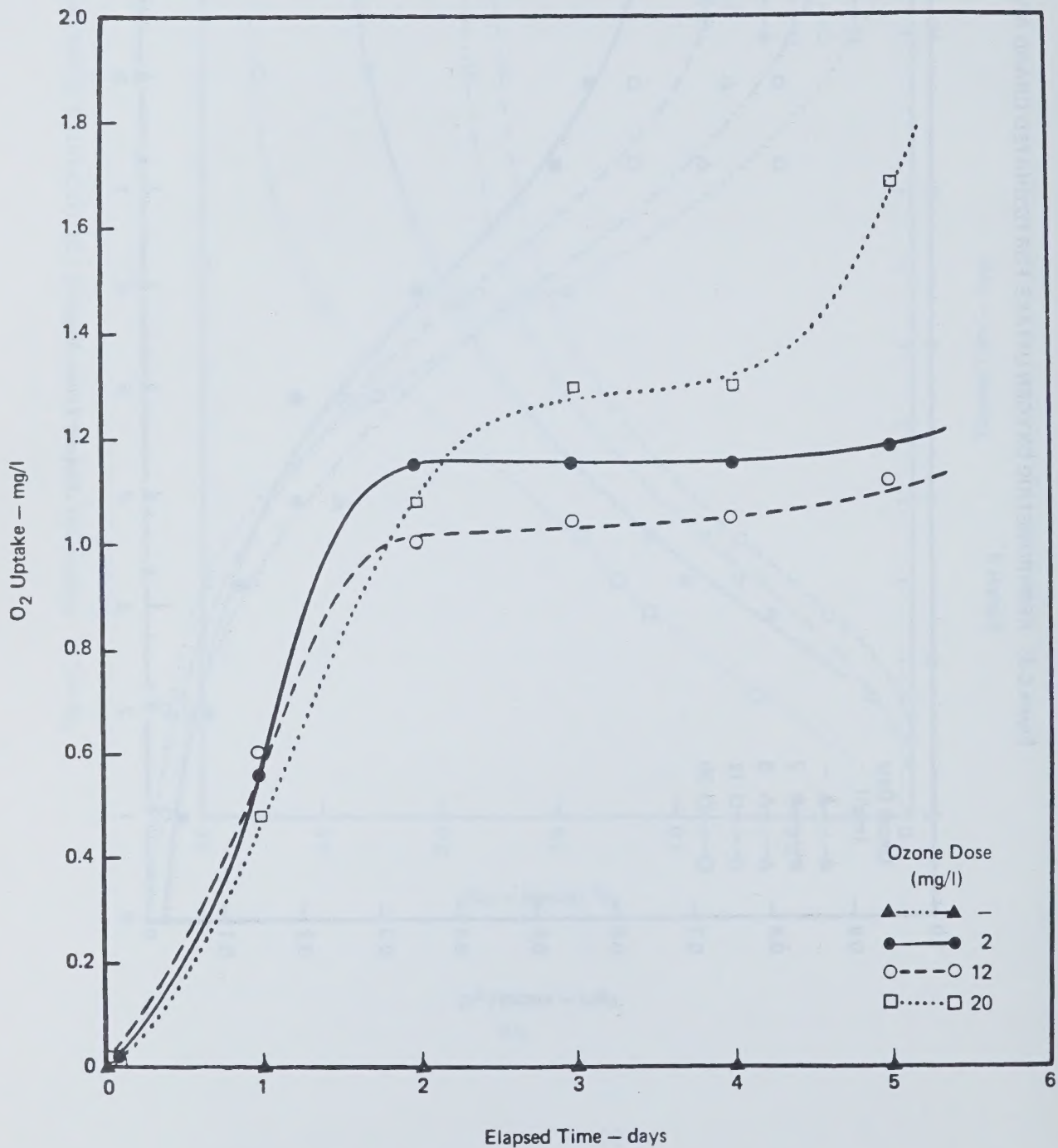


Figure C-5: RESPIROMETRIC OXYGEN UPTAKE FOR OZONATED GRAND RIVER WATER
Sample 5

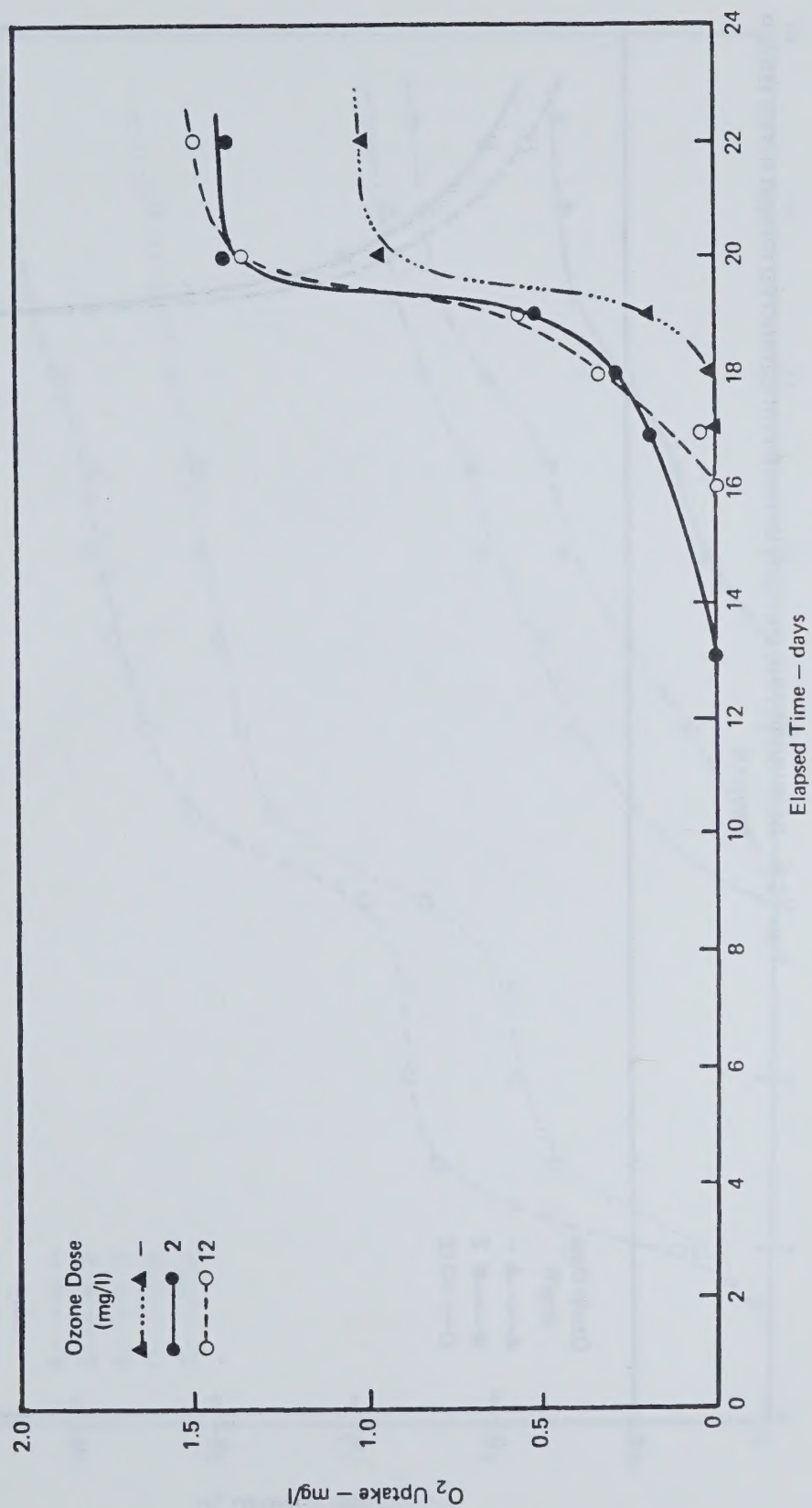


Figure C-6: RESPIROMETRIC OXYGEN UPTAKE FOR OZONATED GRAND RIVER WATER
Sample 6

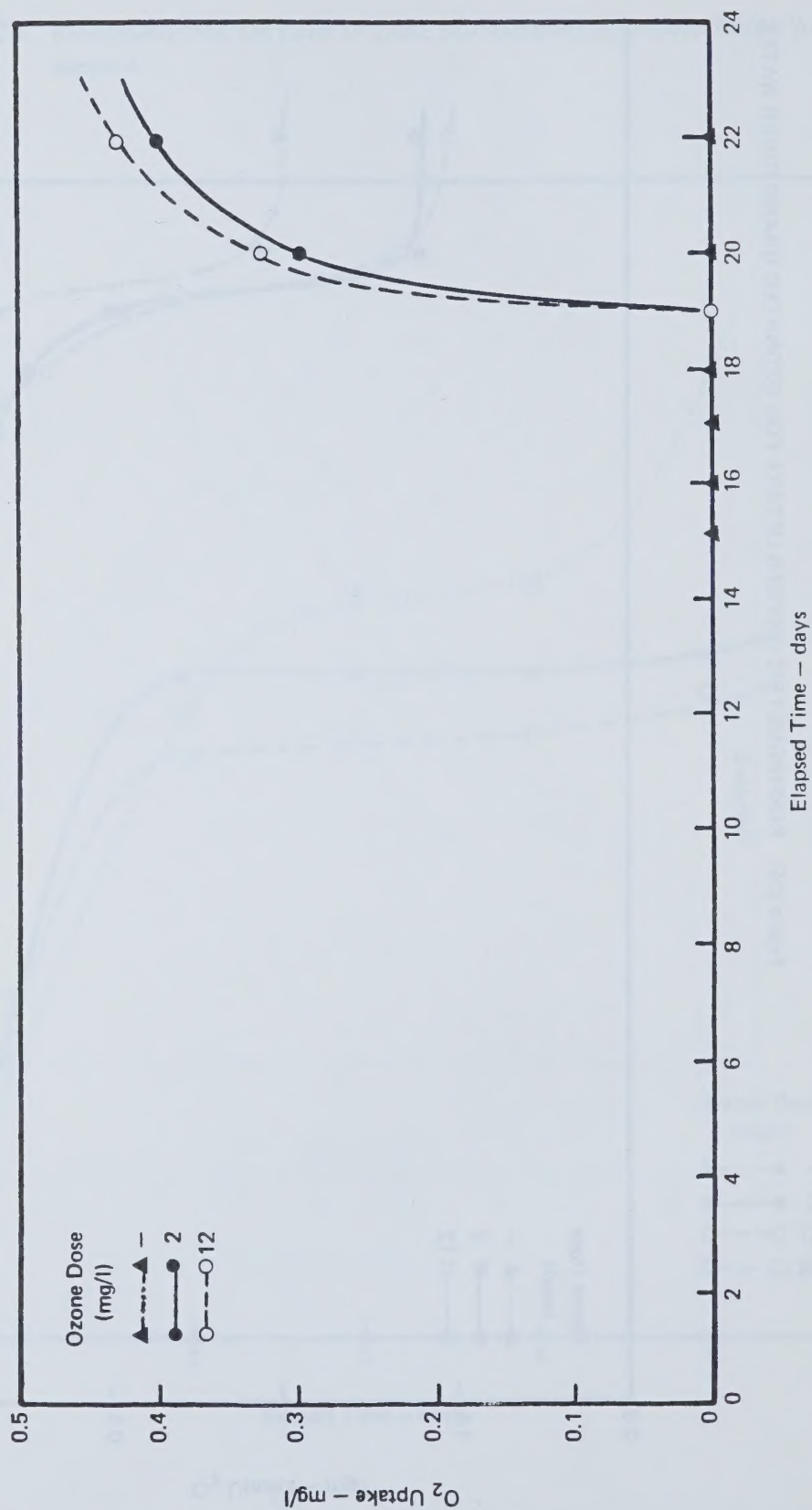


Figure C-7: RESPIROMETRIC OXYGEN UPTAKE FOR OZONATED GRAND RIVER WATER
Sample 7

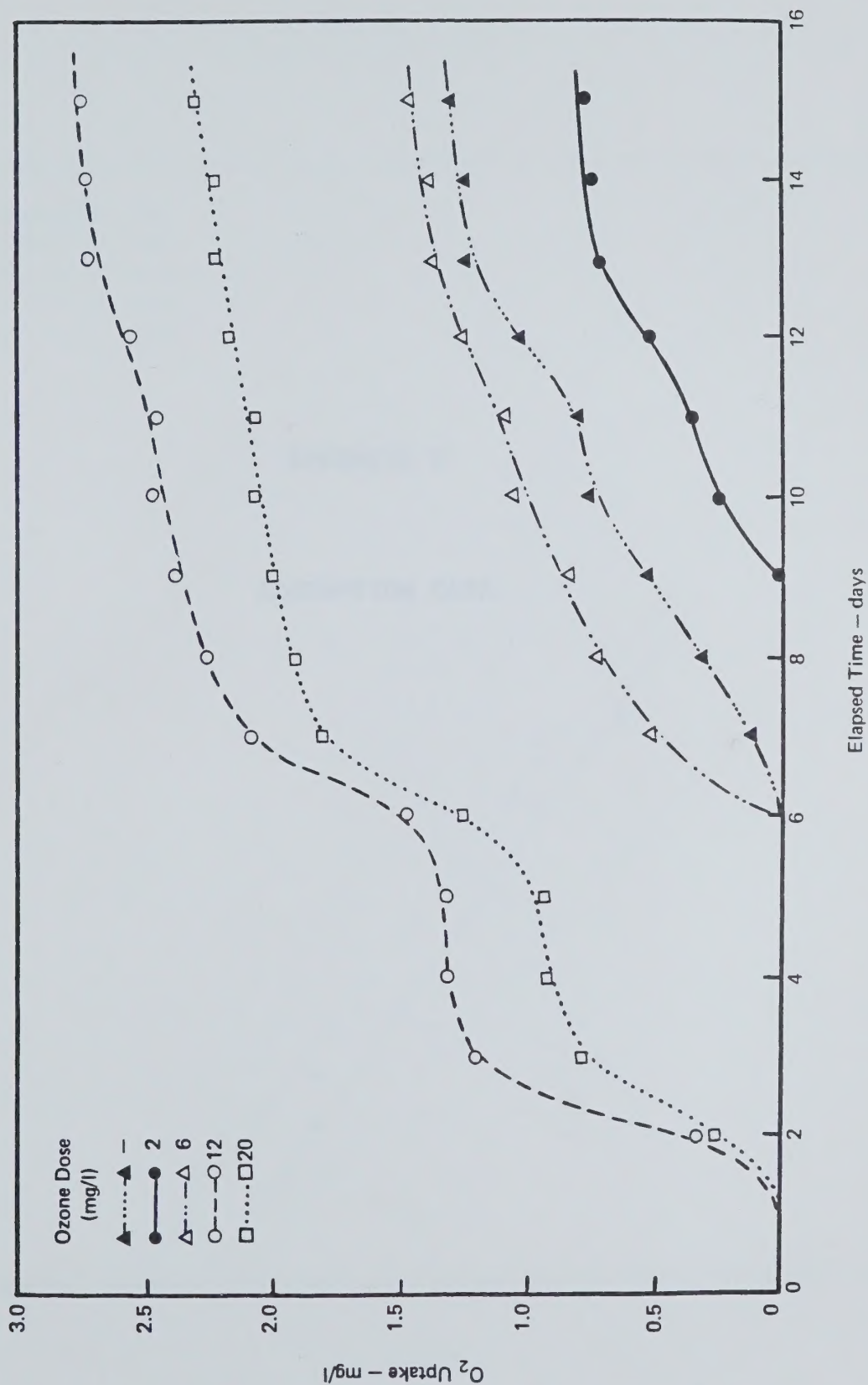


Figure A.1. Adsorption isotherms for the adsorption of benzene vapor on activated carbon at 25°C.



APPENDIX D

ADSORPTION DATA

Figure D-1: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 1: Post-Ozonation

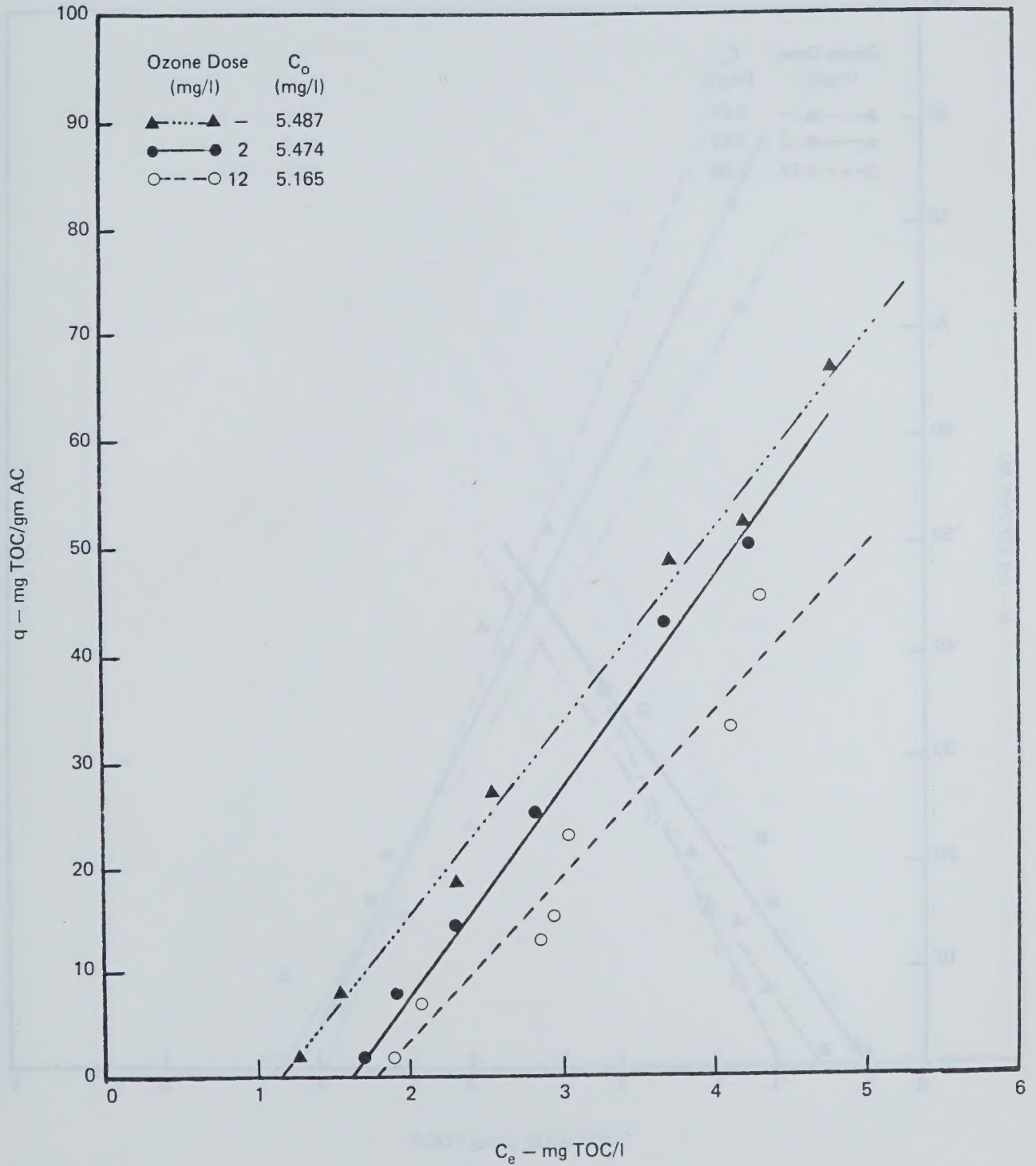


Figure D-2: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 1: Post-Ozonation and Respirometry

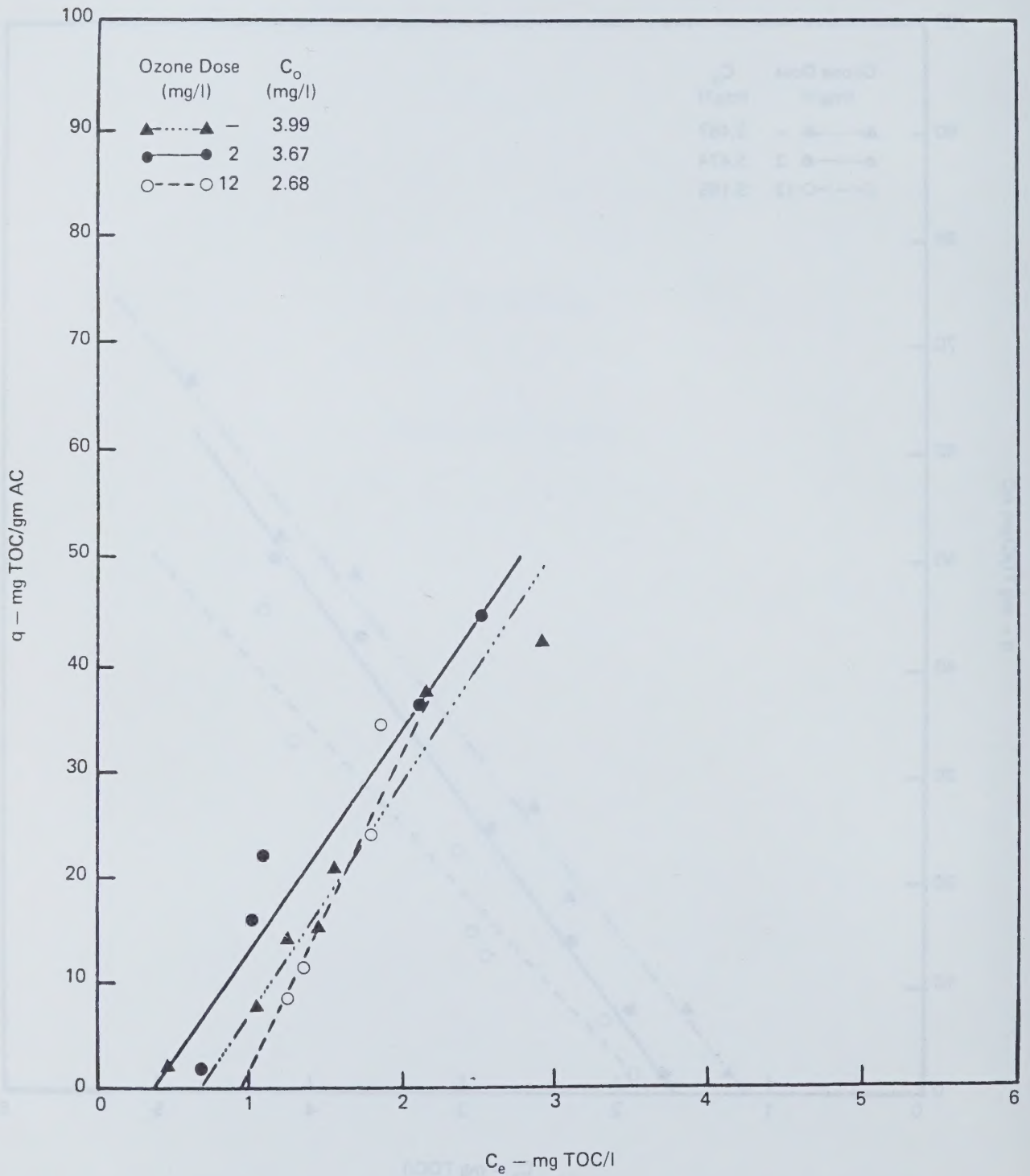


Figure D-3: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 2: Post-Ozonation

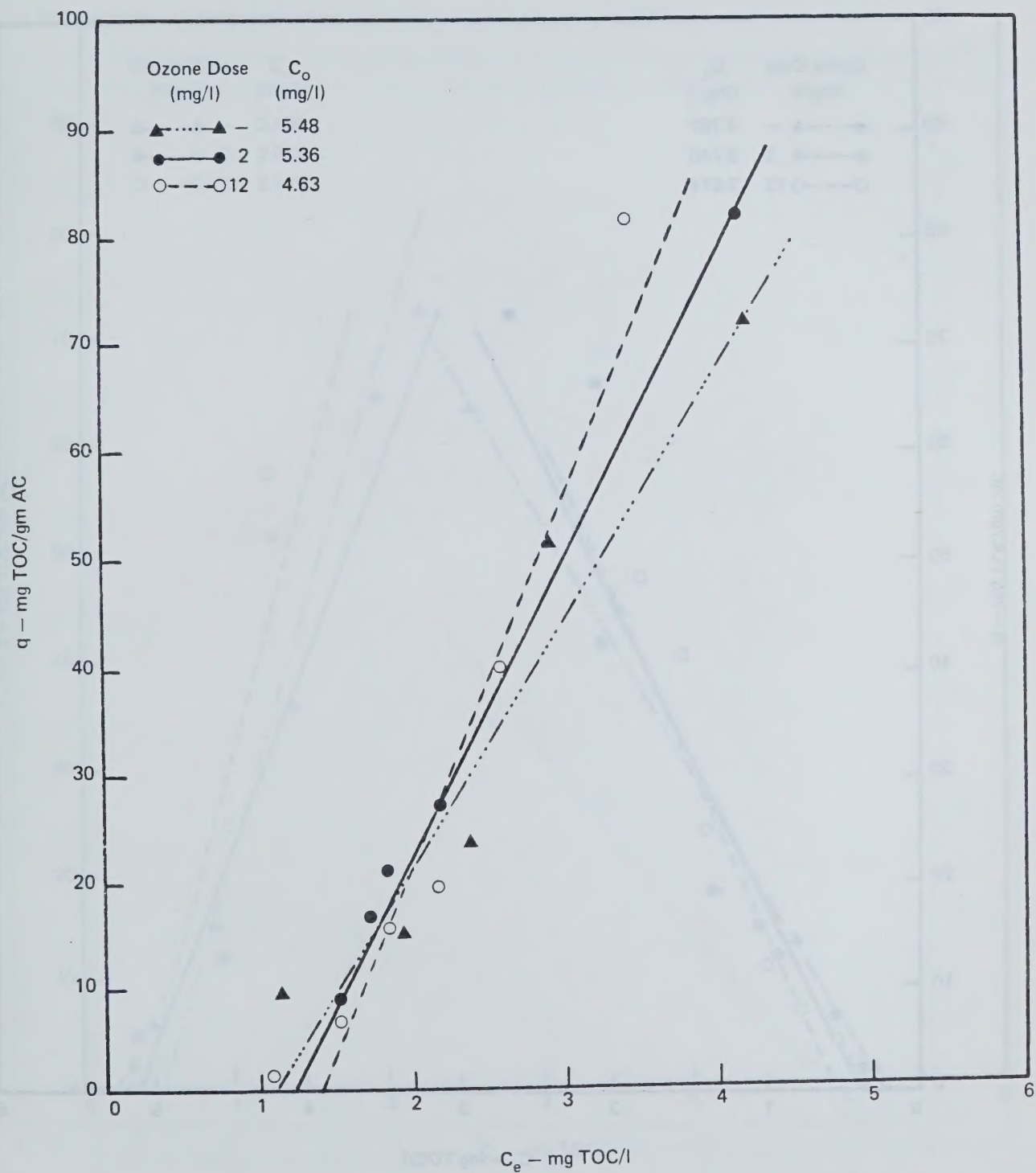


Figure D-4: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 2: Post-Ozonation and Respirometry

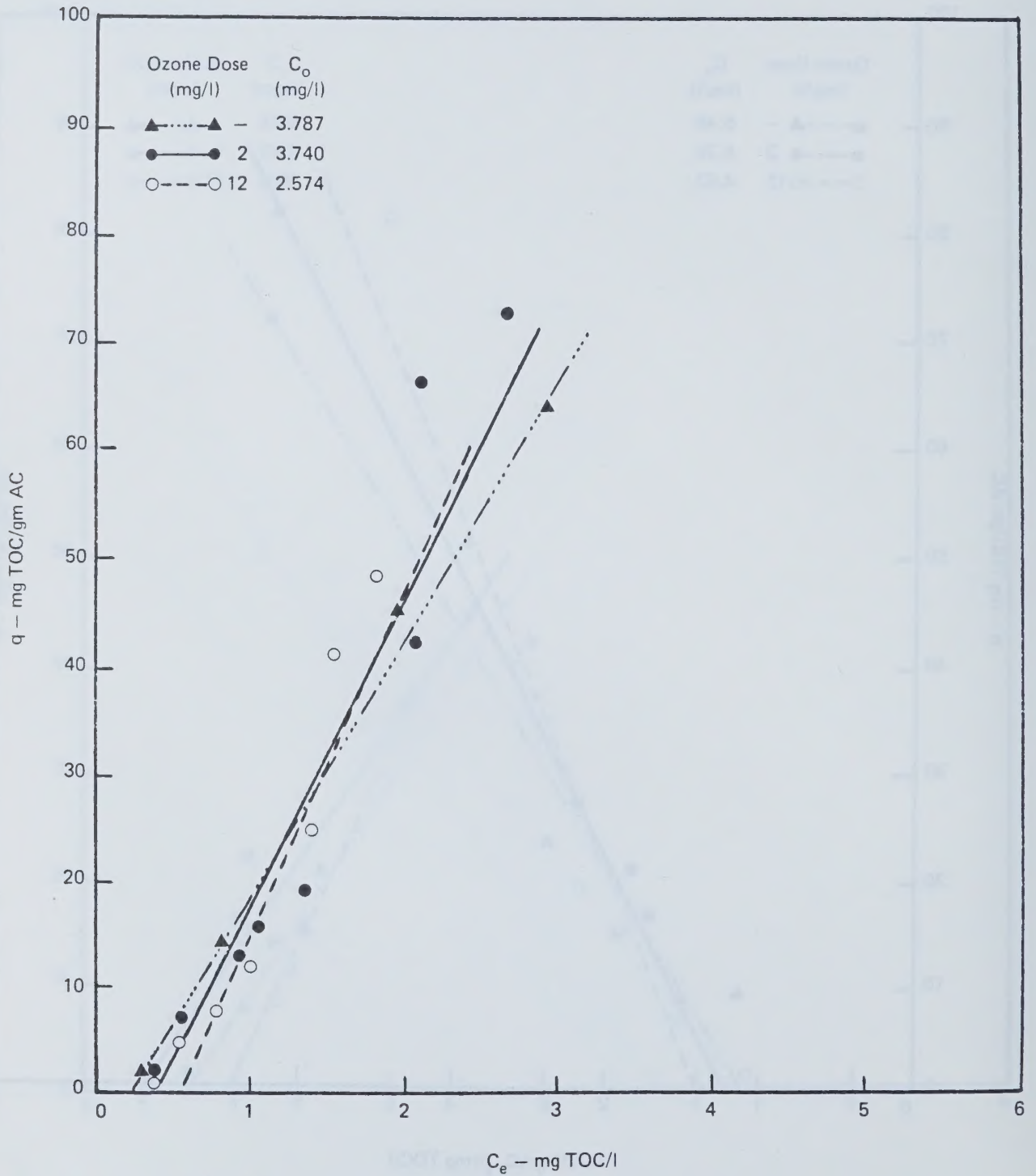


Figure D-5: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 3: Post-Ozonation and Respirometry

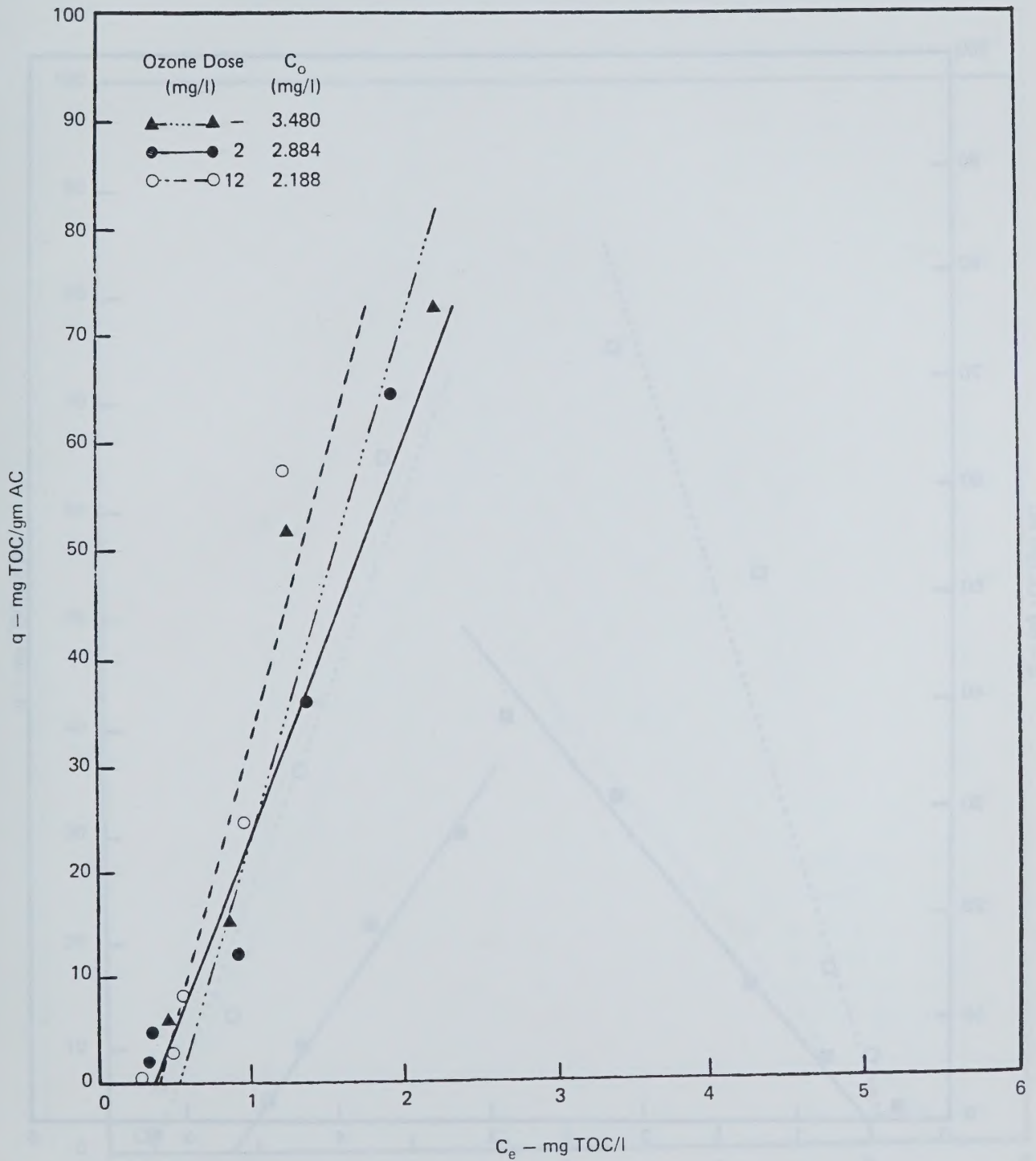


Figure D-6: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 3: Post-Ozonation and Respirometry

Ozone Dose (mg/l)	C_o (mg/l)	Activated Carbon Used
0	3.480	□ F-400 ■ Hydrodarco 3000

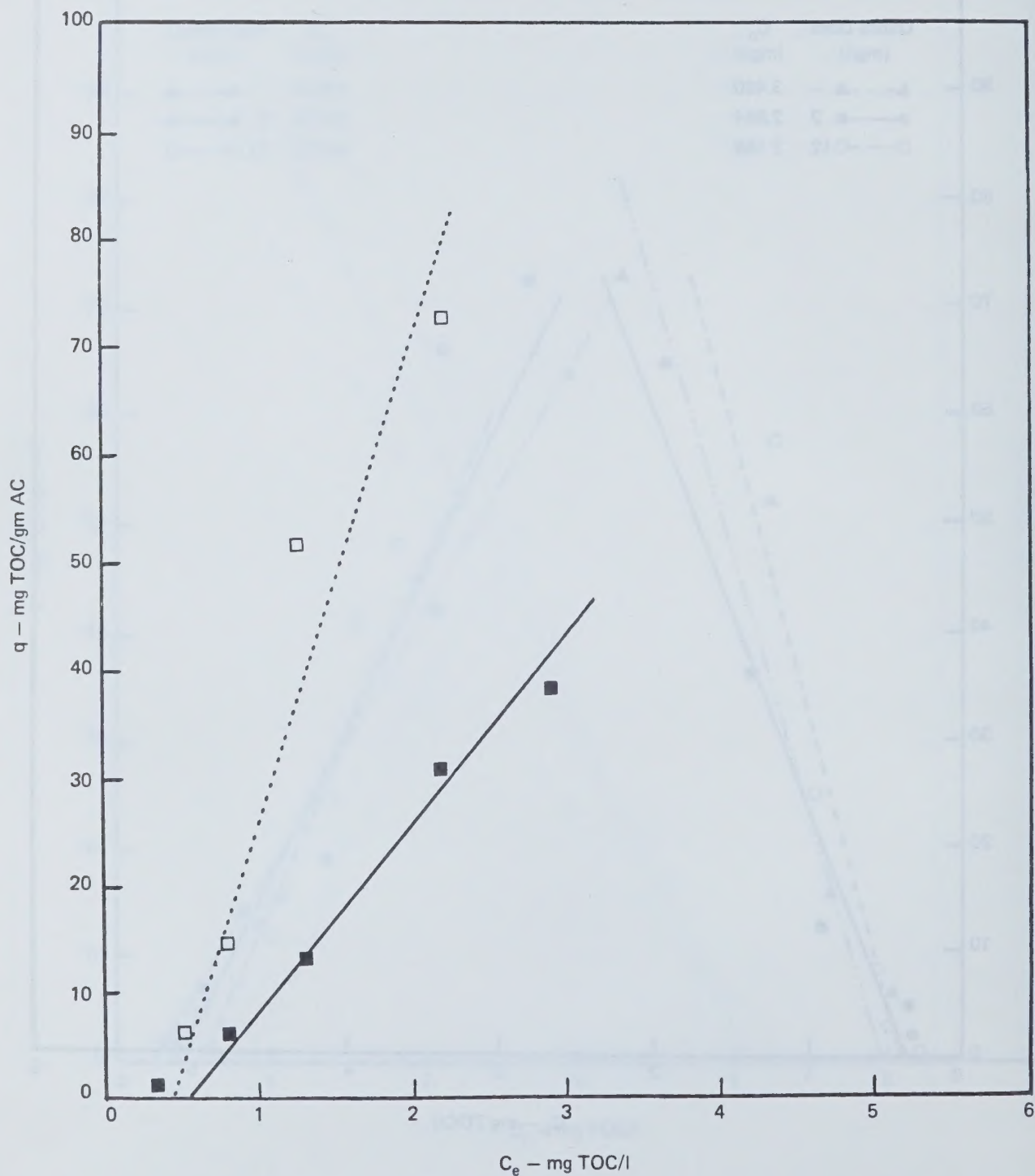


Figure D-7: ACTIVATED CARBON ADSORPTION ISOTHERM

Sample 3: Post-Ozonation and Respirometry

Ozone Dose
(mg/l)

2

C_o
(mg/l)

2.884

Activated Carbon Used

□.....□ F-400

■——■ Hydrodarco 3000

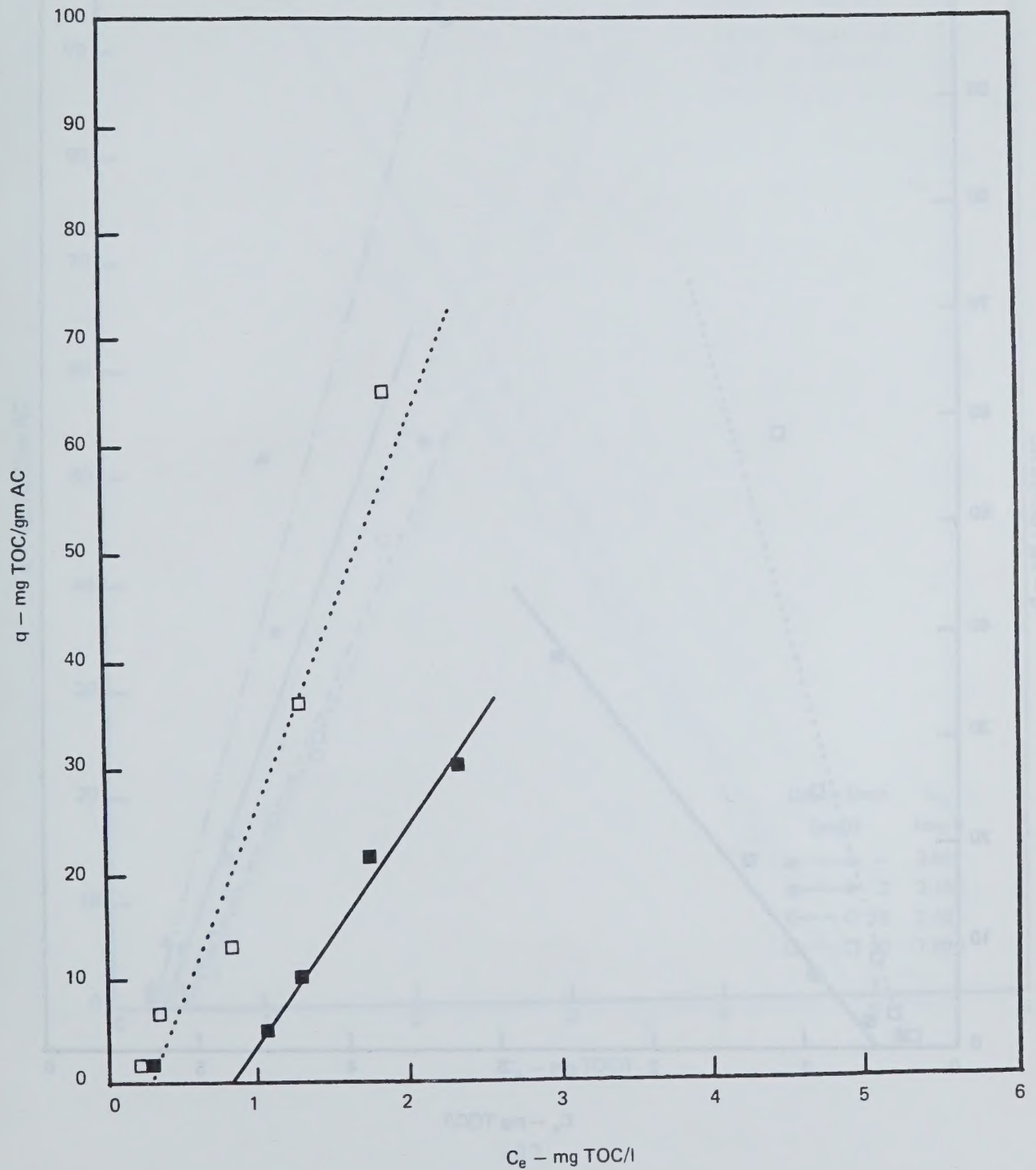


Figure D-8: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 3: Post-Ozonation and Respirometry

Ozone Dose (mg/l)	C_o (mg/l)	Activated Carbon Used
12	2.188	□ F-400 ■ Hydrodarco 3000

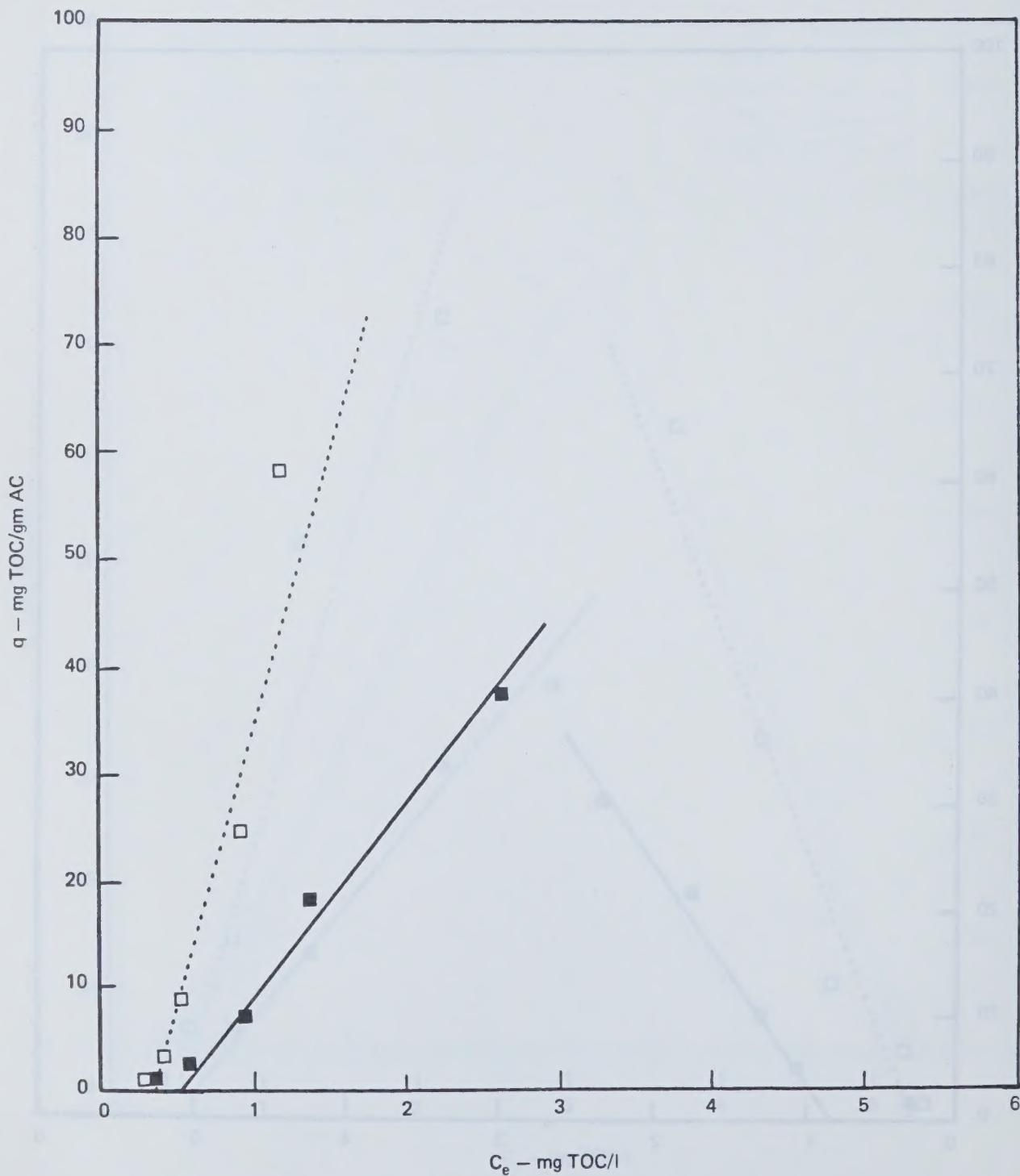


Figure D-9: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 4: Post-Ozonation and Respirometry

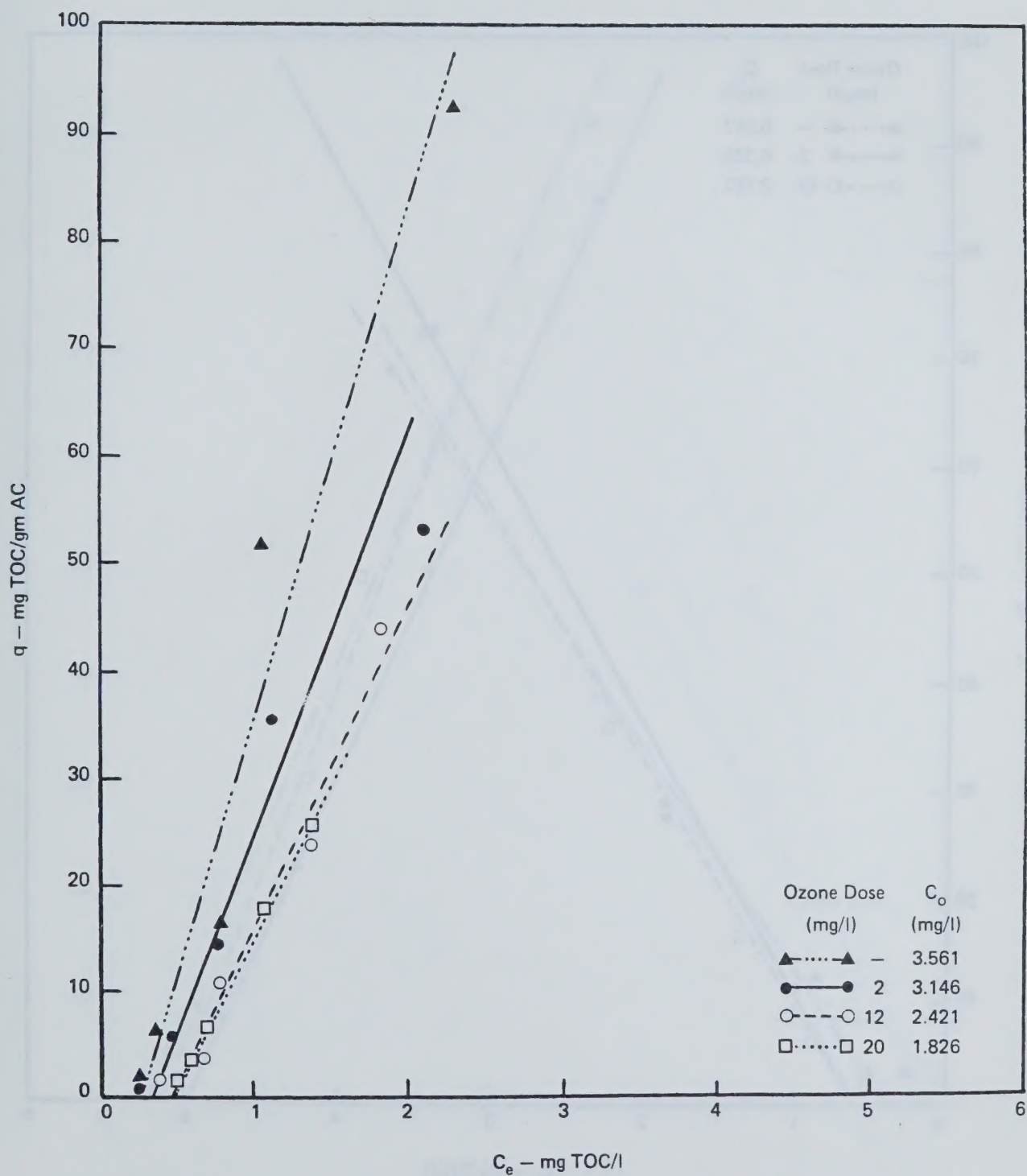


Figure D-10: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 5: Post-Ozonation and Respirometry

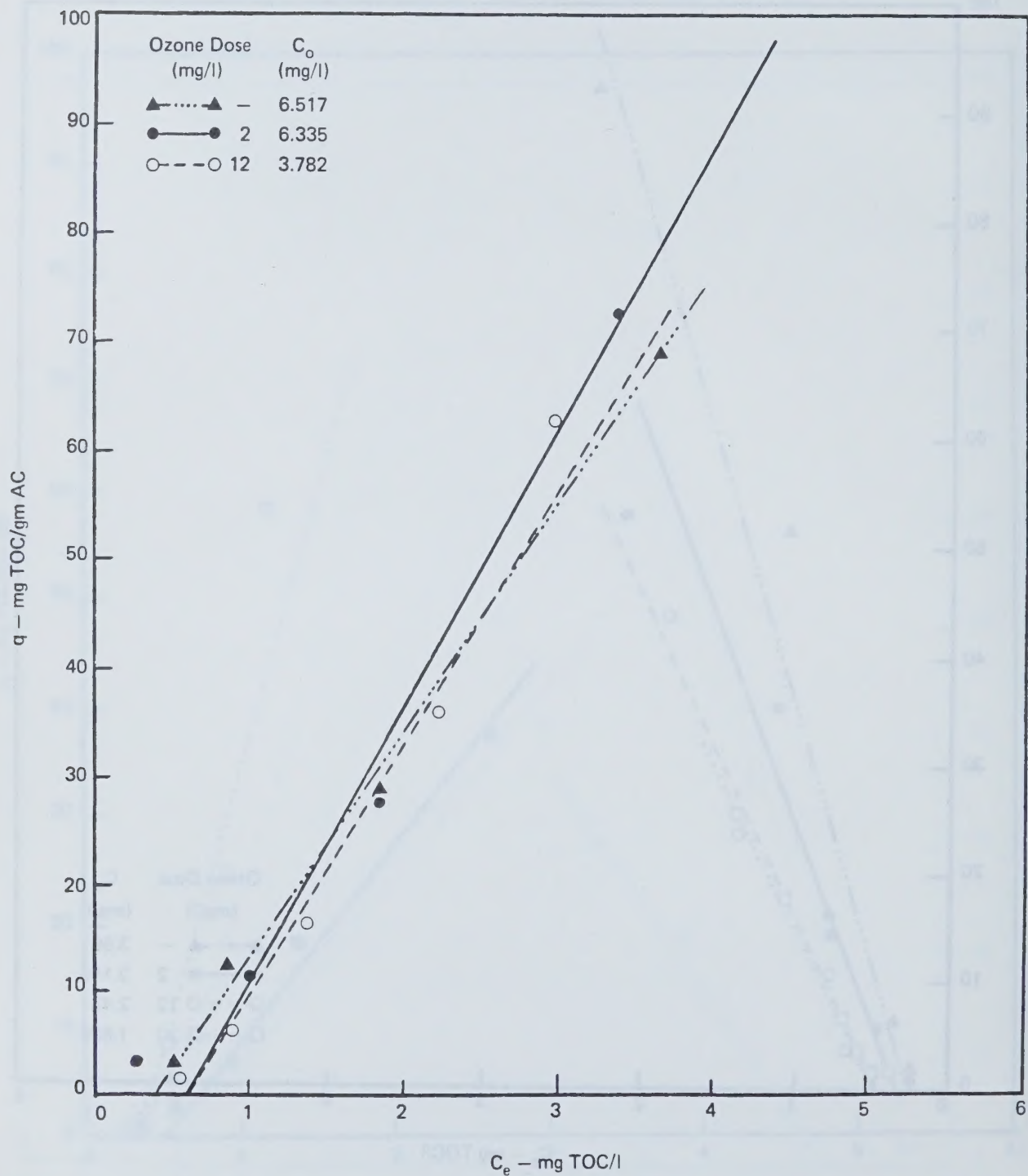


Figure D-11: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 6: Post-Ozonation and Respirometry

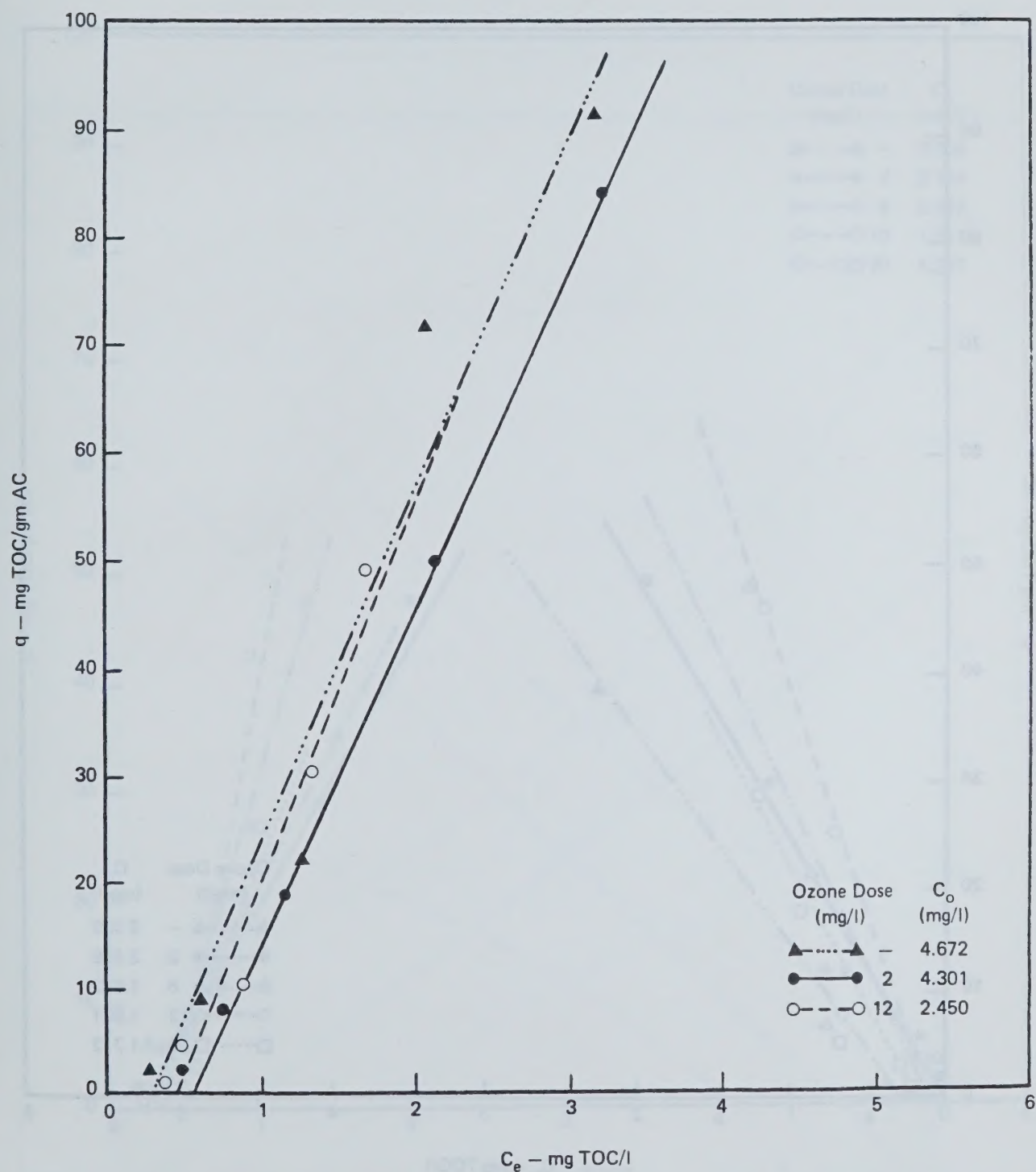


Figure D-12: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 7: Post-Ozonation

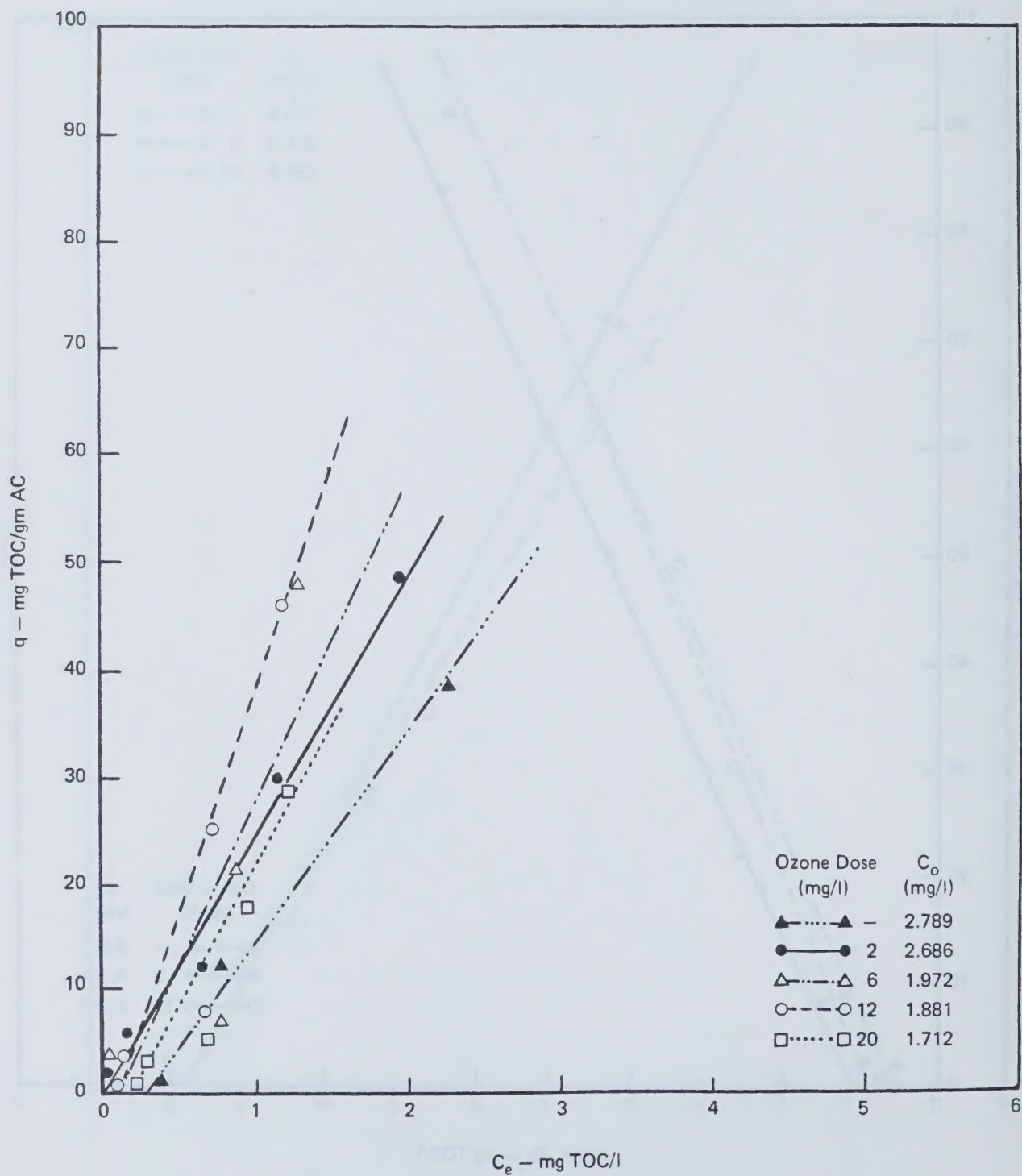


Figure D-13: ACTIVATED CARBON ADSORPTION ISOTHERM
Sample 7: Post-Ozonation and Respirometry

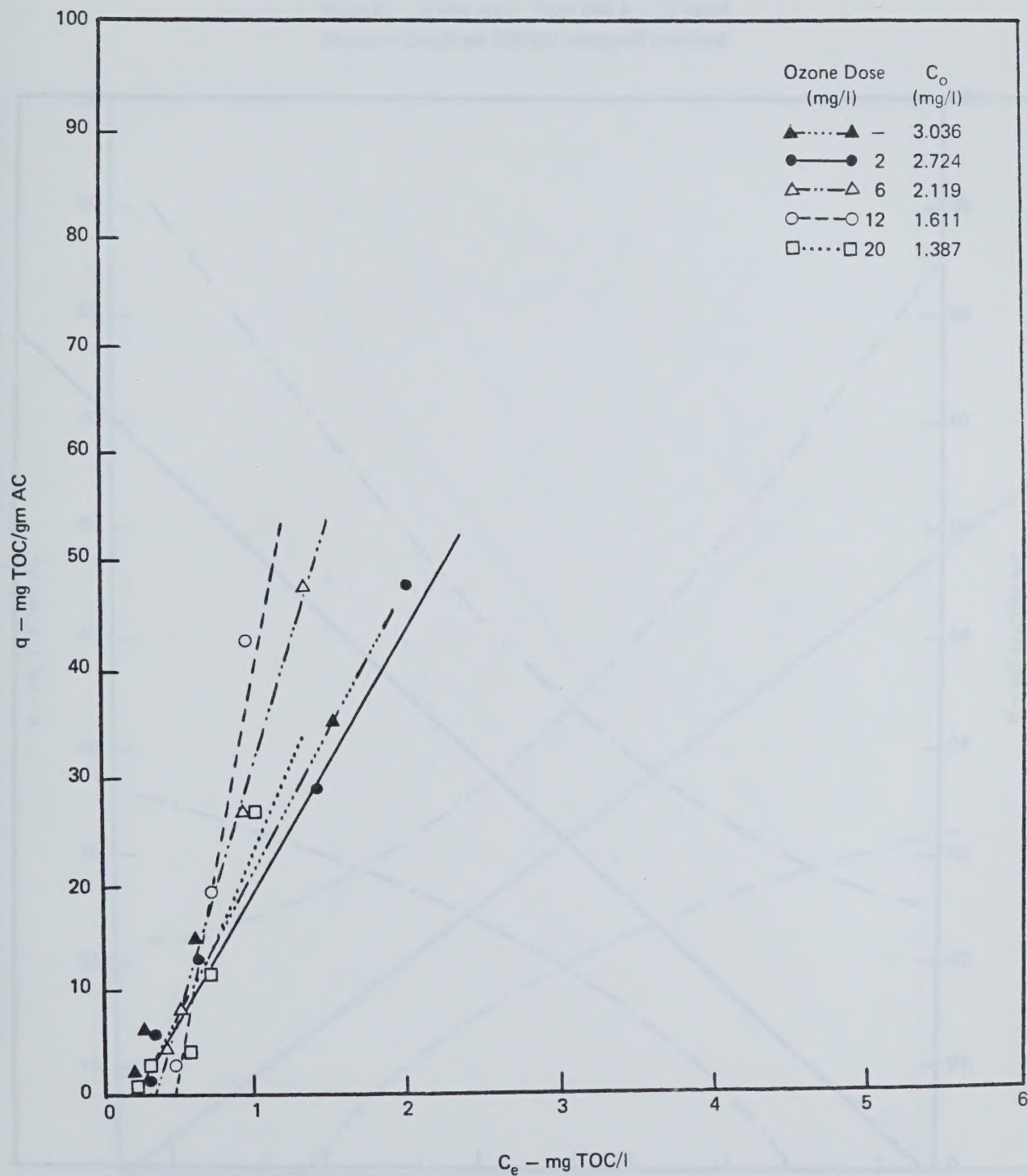


Figure D-14: COMPOSITE ACTIVATED CARBON ADSORPTION ISOTHERM
(LEAST SQUARES FITTED), SHOWING 95% CONFIDENCE LIMITS

Pretreated Samples

Mean C_o : 4.586 mg/l

Standard Deviation : 1.556 for C_o

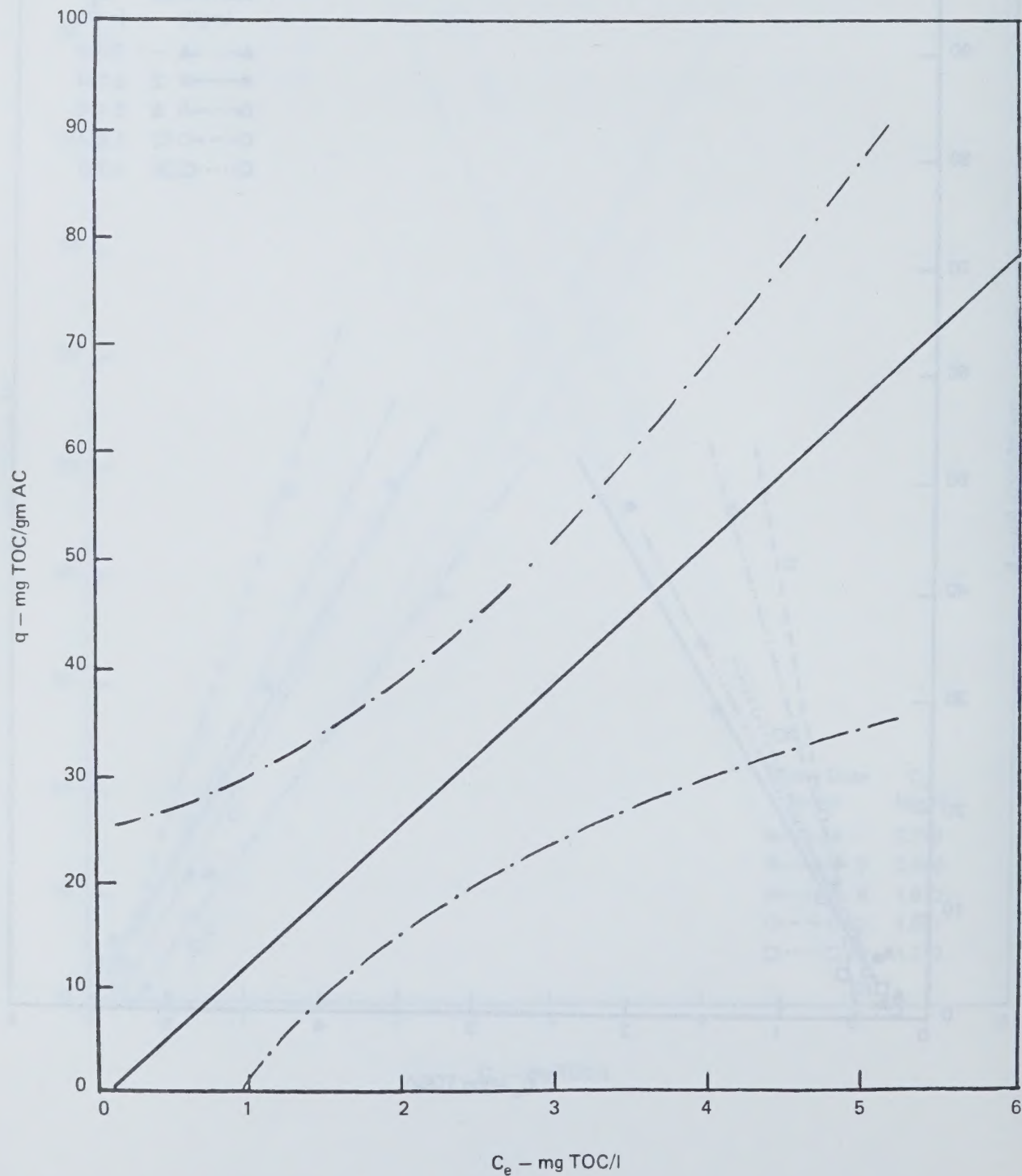


Figure D-15: COMPOSITE ACTIVATED CARBON ADSORPTION ISOTHERM
(LEAST SQUARES FITTED), SHOWING 95% CONFIDENCE LIMITS

Pretreated and Ozonated Samples

Ozone Dose : 12 mg/l

Mean C_0 : 3.894 mg/l

Standard Deviation : 1.763 for C_0

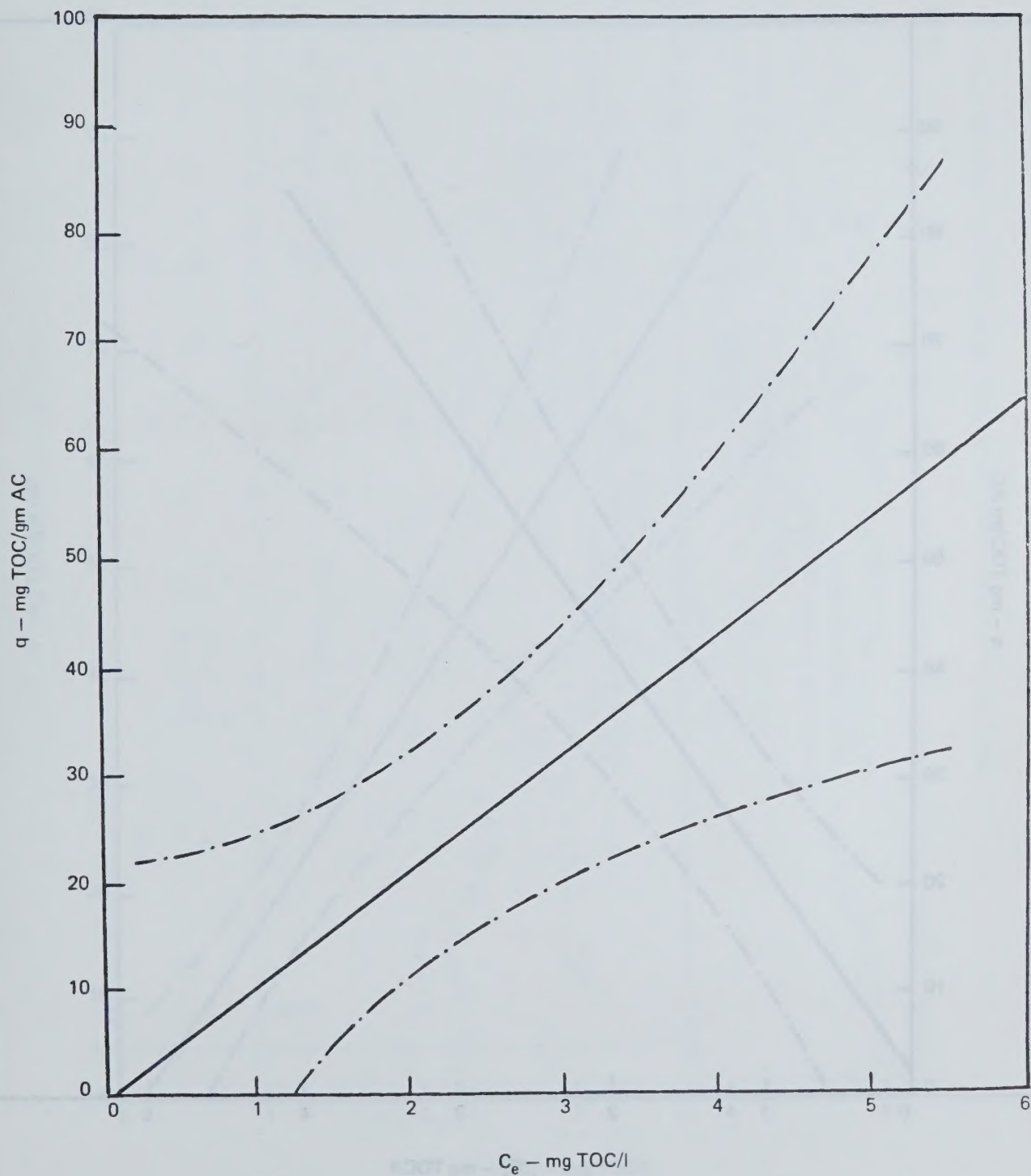


Figure D-16: COMPOSITE ACTIVATED CARBON ADSORPTION ISOTHERM
(LEAST SQUARES FITTED), SHOWING 95% CONFIDENCE LIMITS

Pretreated and Biodegraded Samples

Mean C_o : 4.143 mg/l

Standard Deviation : 1.156 for C_o

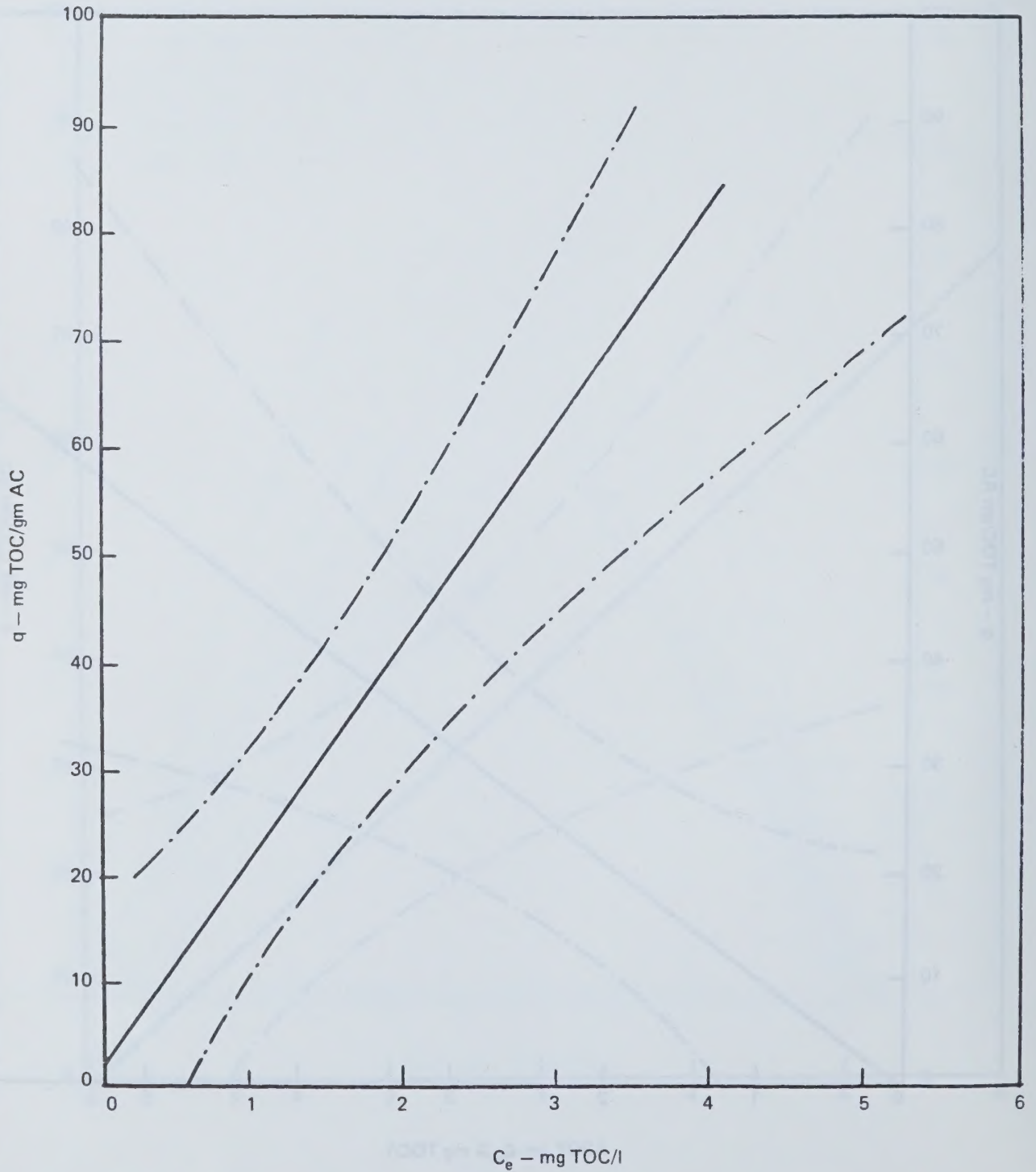


Figure D-17: COMPOSITE ACTIVATED CARBON ADSORPTION ISOTHERM
(LEAST SQUARES FITTED), SHOWING 95% CONFIDENCE LIMITS

Pretreated, Ozonated and Biodegraded Samples

Ozone Dose : 12 mg/l

Mean C_o : 2.511 mg/l

Standard Deviation : 0.738 for C_o

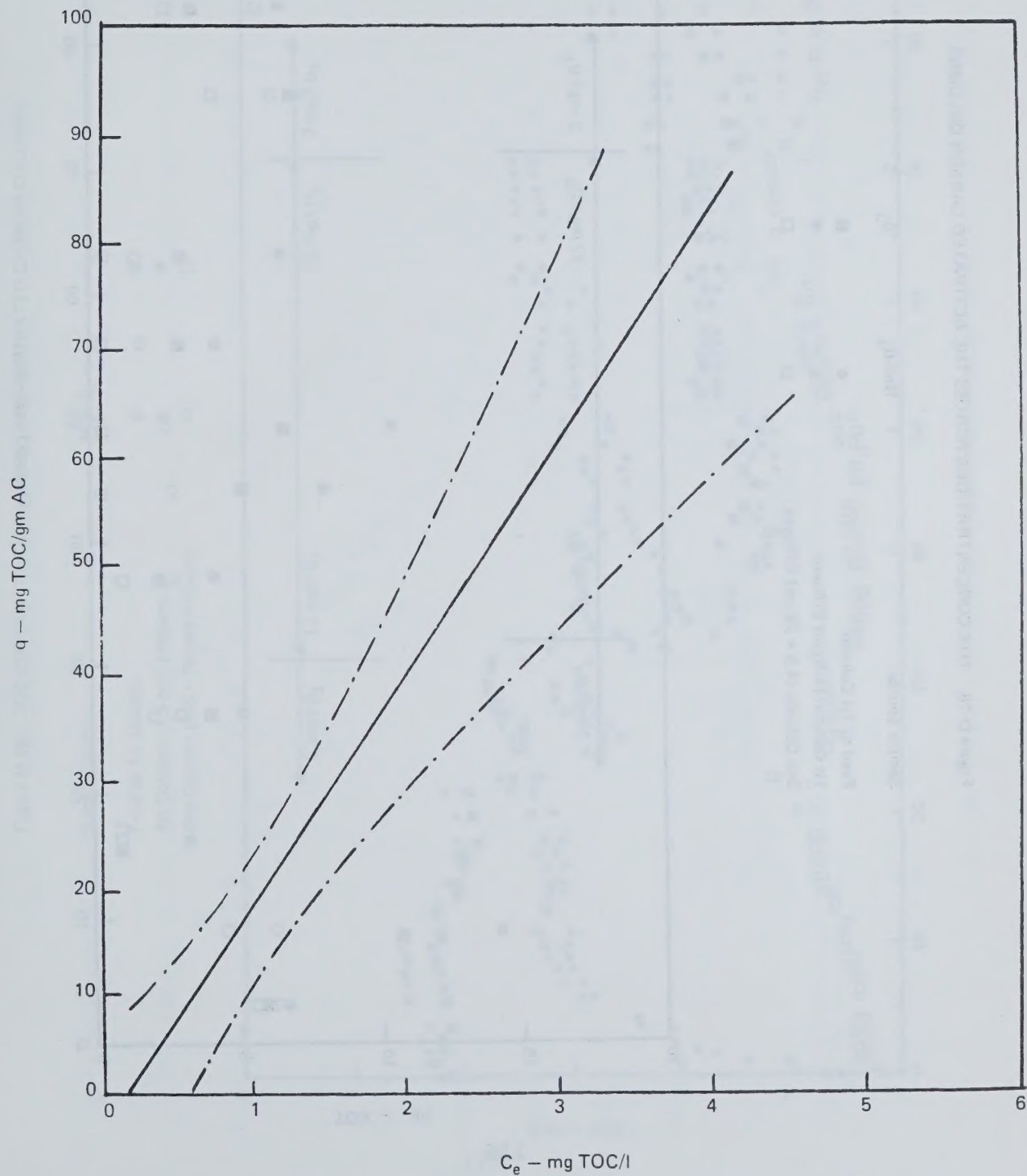


Figure D-18: TOX CONCENTRATIONS ACROSS THE ACTIVATED CARBON COLUMNS

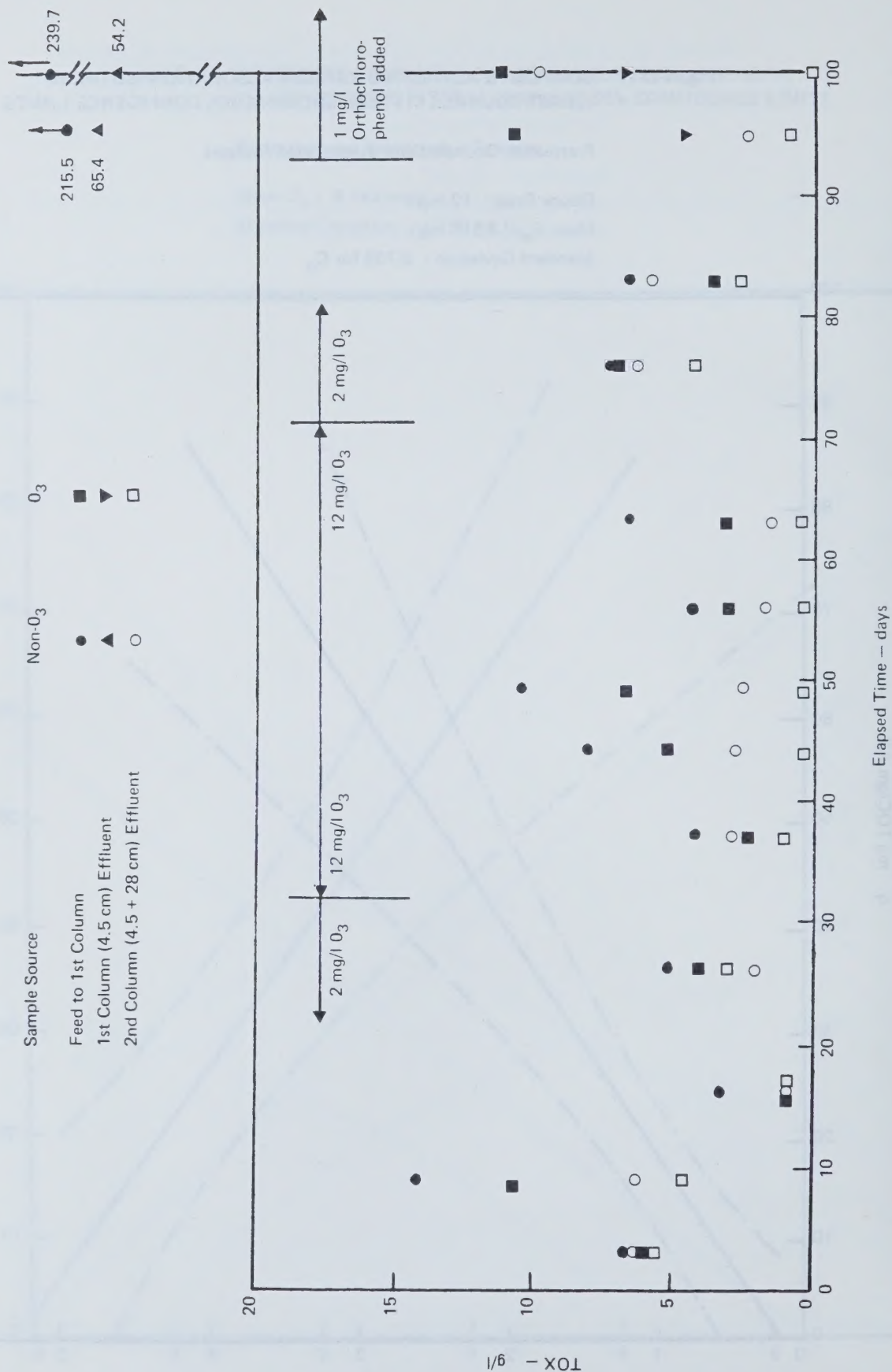


Figure D-19: TOC CONCENTRATION ACROSS THE ACTIVATED CARBON COLUMNS

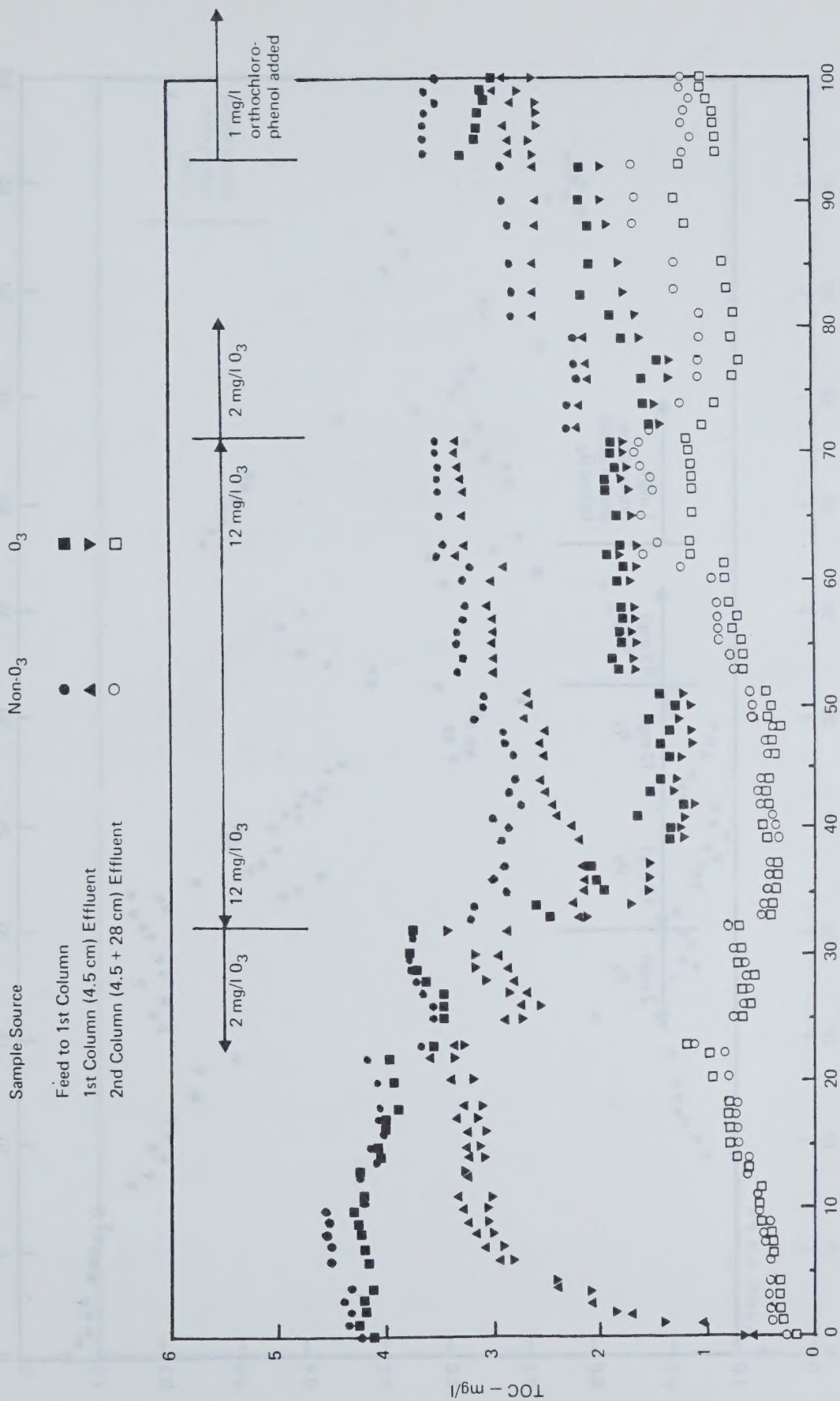


Figure D-20: COLUMN BREAKTHROUGH AT THE 4.5 + 28 cm BED DEPTH WITH OZONATED WATER

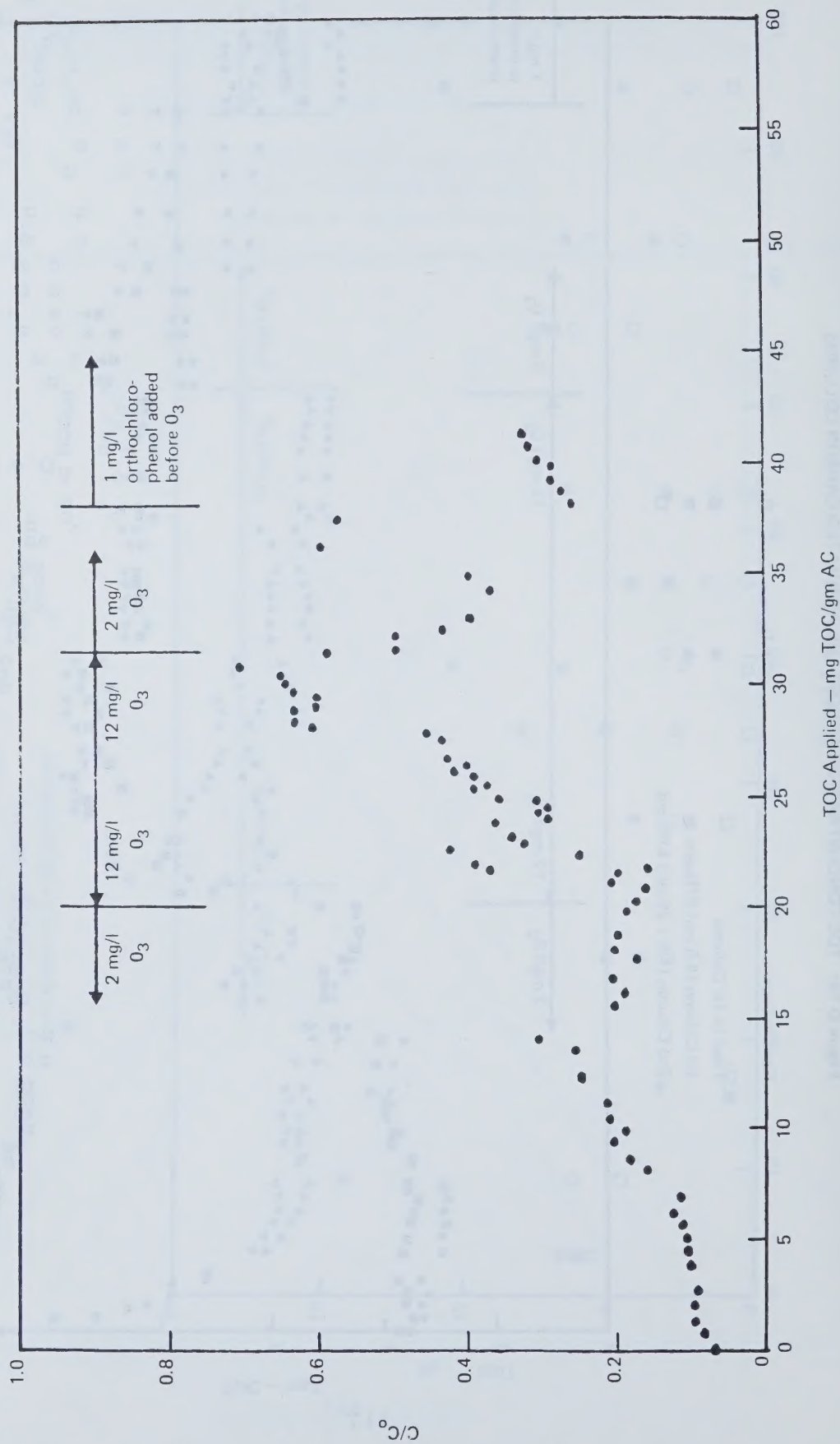
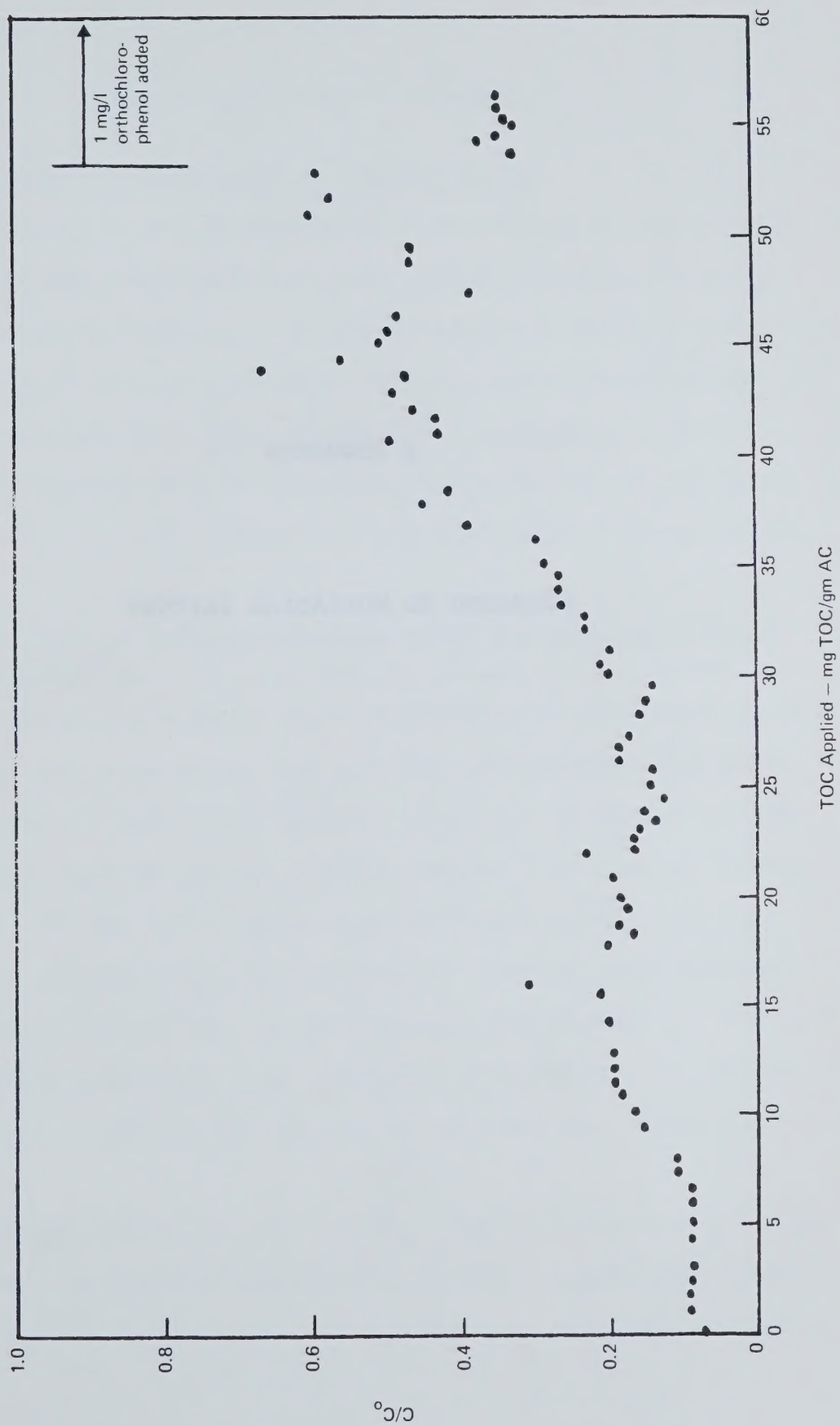


Figure D-21: COLUMN BREAKTHROUGH AT THE 4.5 + 28 cm BED DEPTH WITH NON-OZONATED WATER



APPENDIX E

PARTIAL OXIDATION OF ORGANICS

E.1 EFFECT OF TEMPERATURE ON CO₂/VOC RATIO

Experiments were conducted to determine the effect of temperature on the CO₂/VOC ratio in the effluent stream under various conditions. This is illustrated in Figure E-1 which is based on averaged data. From this it may be concluded that the relative efficiency in CO₂ is greater than that for VOC for a specific organic and that lower temperatures favor oxidation of the more volatile compounds which are more difficult to oxidize at higher temperatures.

APPENDIX E

PARTIAL OXIDATION OF ORGANICS

E.1 Partial Oxidation of Organic Compounds

Experiments were conducted to determine the effect of temperature on the CO₂/VOC ratio in the effluent stream under various conditions. This is illustrated in Figure E-1 which is based on averaged data. From this it may be concluded that the relative efficiency in CO₂ is greater than that for VOC for a specific organic and that lower temperatures favor oxidation of the more volatile compounds which are more difficult to oxidize at higher temperatures.

The overall change in CO₂ ratio, due to temperature, provides a measure of the effect of temperature on the oxidation of organic compounds. This is shown in Figure E-2 which is based on averaged data.

APPENDIX E

PARTIAL OXIDATION OF ORGANICS

E.1 Effect of Ozonation on COD:TOC Ratio

Ozonation was found to result in a reduction of the COD:TOC ratios in the water samples under investigation. This is illustrated in Figure E-1 which is based on averaged data. From this it may be concluded that the relative reduction in COD is greater than that of TOC for a specific ozone dose and that those organics remaining after ozonation are more oxidized than those present in the water prior to ozonation.

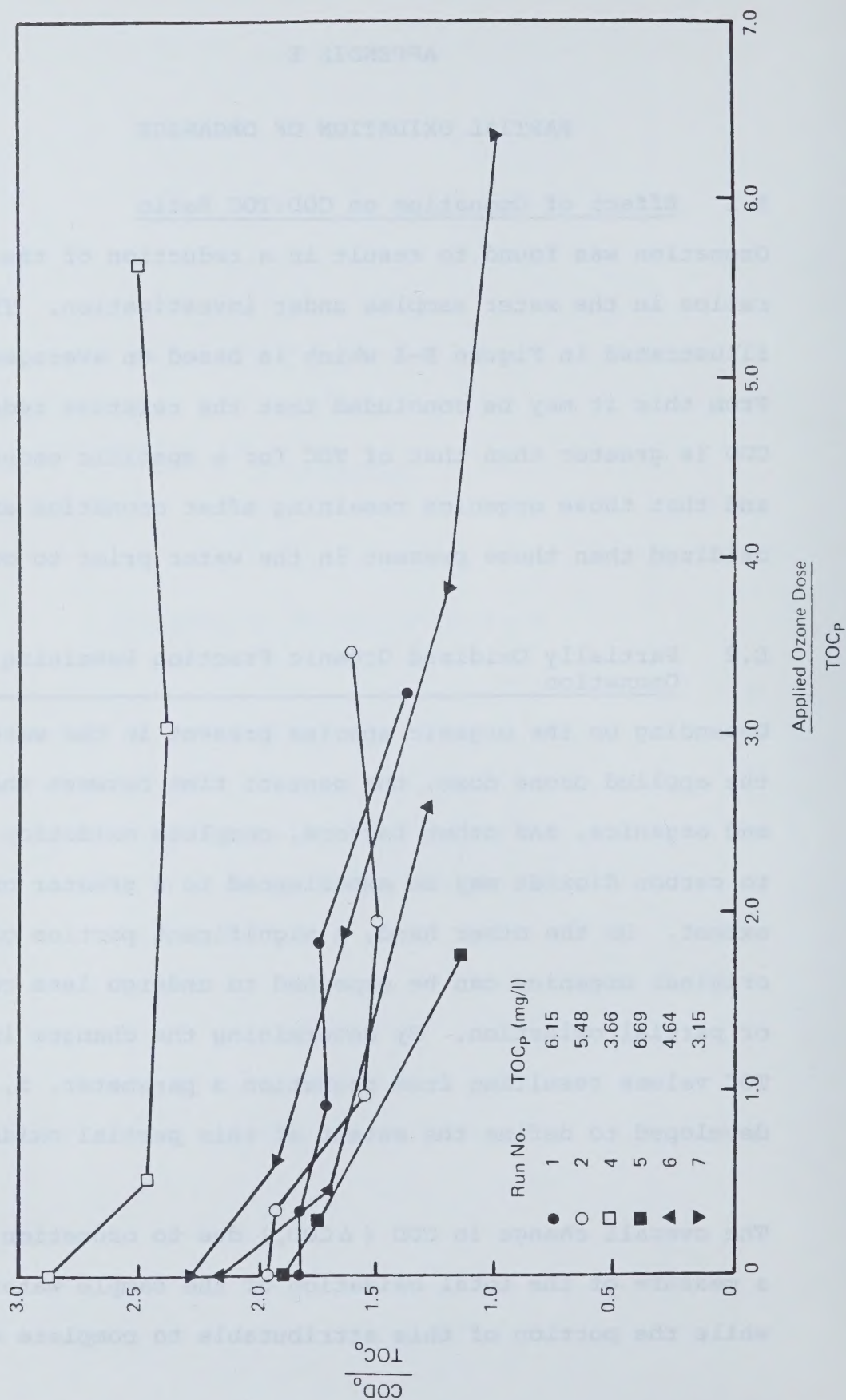
E.2 Partially Oxidized Organic Fraction Remaining After Ozonation

Depending on the organic species present in the water sample, the applied ozone dose, the contact time between the ozone and organics, and other factors, complete oxidation of TOC to carbon dioxide may be experienced to a greater or lesser extent. On the other hand, a significant portion of the original organics can be expected to undergo less complete or partial oxidation. By determining the changes in COD and TOC values resulting from ozonation a parameter, f , may be developed to define the extent of this partial oxidation.

The overall change in COD (ΔCOD_o) due to ozonation provides a measure of the total oxidation of the sample water organics, while the portion of this attributable to complete oxidation

Figure E-1: COD/TOC RATIO AFTER OZONATION ($\text{COD}_o/\text{TOC}_o$)
vs APPLIED OZONE DOSE PER UNIT INITIAL TOC (TOC_p)

GRAND RIVER



to carbon dioxide may be determined from the change in TOC (ΔTOC_o). The parameter, f , may then be defined as follows:

$$f = \frac{\Delta\text{COD}_o - X \cdot \Delta\text{TOC}_o}{\text{COD}_o} \quad (\text{E-1})$$

where:

f = fraction of COD partially oxidized

COD_o = COD after ozonation

ΔCOD_o = change in COD due to ozonation

ΔTOC_o = change in TOC due to ozonation

X = a constant, expressing TOC removal as an equivalent reduction in COD

The value of the constant, X , is specific to the particular water source and, as shown in E.2 below, has been estimated for present purposes at 2.62 for the Grand River water samples under investigation.

E.3 TOC Oxygen Demand Equivalent, X

In order to calculate the fraction of partially oxidized organics after ozonation as defined by Equation E-1, the constant, X , expressing TOC removal as an equivalent reduction in COD must be known. The value of X has been calculated based on the following assumptions.

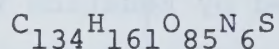
- i) The composition of organics in the Grand River water samples is assumed to be essentially similar to that of humic substances (HS).

- ii) The oxygen demand of nitrogen is not recorded in the COD test.
- iii) The oxygen demand for the oxidation of sulphur is negligible.
- iv) Selected oxidation of specific functional groups is neglected.
- v) TOC removal results from the oxidation of carbon to carbon dioxide.

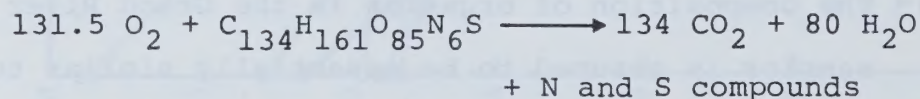
According to Schnitzer and Khan (1972), the mean composition of humic substances (HS) may be specified as follows:

Element	% by wt.	Moles/100 gm HS
C	50	4.17
O	42	2.63
H	5	5.00
N	2.5	0.18
S	0.5	0.016

The approximate mean molecular composition would therefore be:



The complete oxidation of this compound (ignoring that of nitrogen and sulphur) may then be written as:



From the latter, 131.5 moles of oxygen are required to oxidize 134 moles of carbon to carbon dioxide. Accordingly, the TOC oxygen demand equivalent, X, for the organics present in the water samples may be approximated.

$$X = \frac{131.5 \times 32}{134 \times 12} = 2.62 \text{ mg O}_2/\text{mg TOC}$$

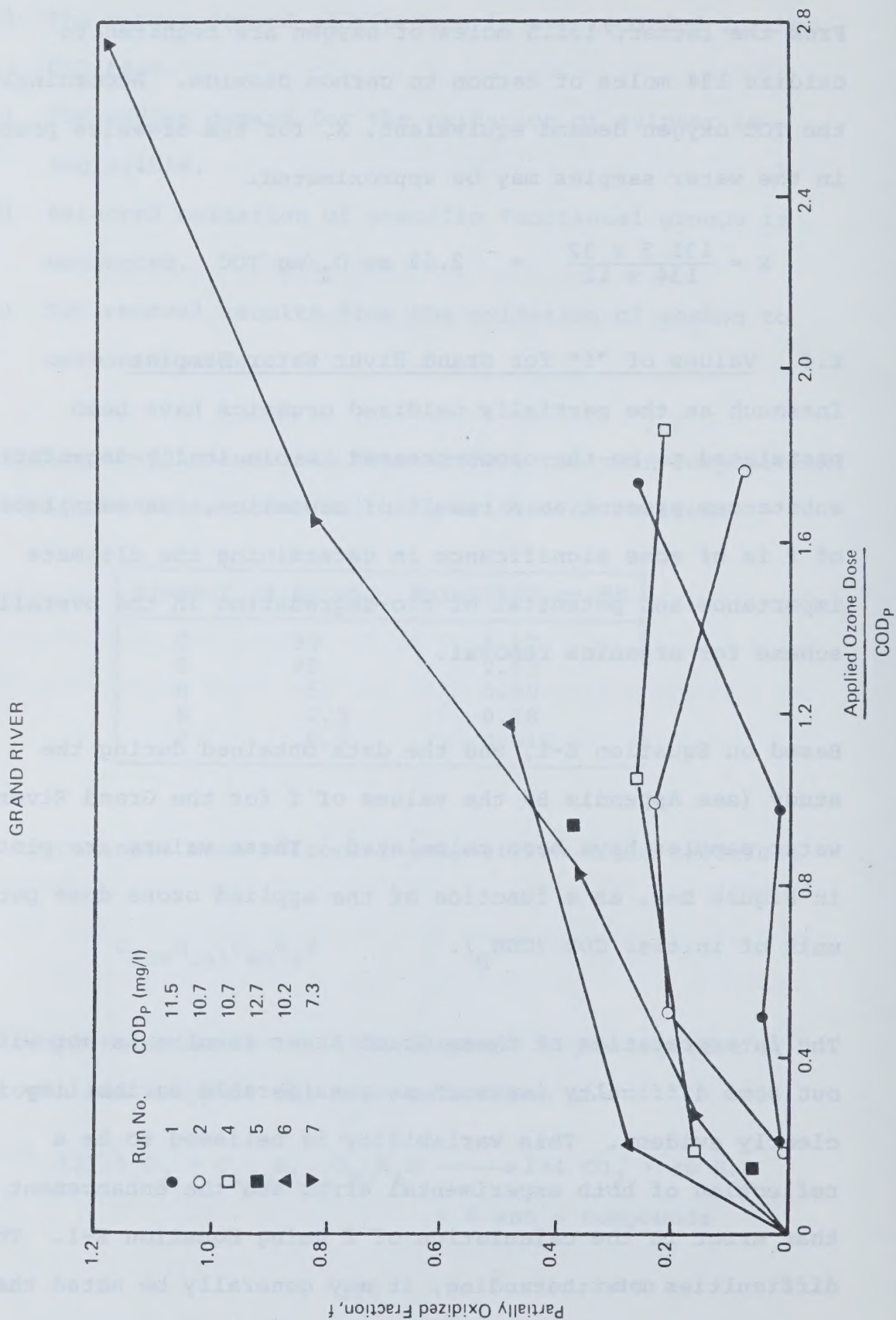
E.4 Values of "f" for Grand River Water Samples

Inasmuch as the partially oxidized organics have been postulated to be the ozone-created, biologically-degradable substances present as a result of ozonation, the magnitude of f is of some significance in determining the ultimate importance and potential of bio-degradation in the overall scheme for organics removal.

Based on Equation E-1, and the data obtained during the study (see Appendix B) the values of f for the Grand River water samples have been calculated. These values are plotted, in Figure E-2, as a function of the applied ozone dose per unit of initial COD (COD_p).

The interpretation of these Grand River results is not without some difficulty inasmuch as considerable variability is clearly evident. This variability is believed to be a reflection of both experimental error and the enhancement of that error in the calculation of f using Equation E-1. Those difficulties notwithstanding, it may generally be noted that

Figure E-2: PARTIALLY OXIDIZED ORGANIC FRACTION, f
vs APPLIED OZONE DOSE PER UNIT INITIAL COD (COD_P)



the oxidized fraction is increased by ozonation and that, in the case of these particular Grand River water samples, the limiting value of f appears to be approximately 0.2 to 0.25.

E.5 Appendix E Reference

Schnitzer, M., and Khan, S.U.,
Humic Substances in the Environment.
Marcel Dekker, Inc., N.Y., 1972

CA1 HW 1179E45

Canada. DNHW. EHD.

79-EHD-45

THE REMOVAL OF ORGANICS FROM DRINKING WATER
BY OZONATION, BIODEGRADATION AND ACTIVATED CARBON
ADSORPTION. 1979. The Removal of Organics

RESOURCE CENTRE
INST. FOR ENVIRON'L. STUDIES
UNIVERSITY OF TORONTO



